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Ergothioneine and related Histidine Derivatives in the Gas Phase: Tautomer Structures determined by IRMPD Spectroscopy and Theory†

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†Electronic supplementary information (ESI) available: additional tandem MS spectra, tables with the band origins of the computed molecular ion structures and coordinates of the ion structures identified by theory.

Abstract

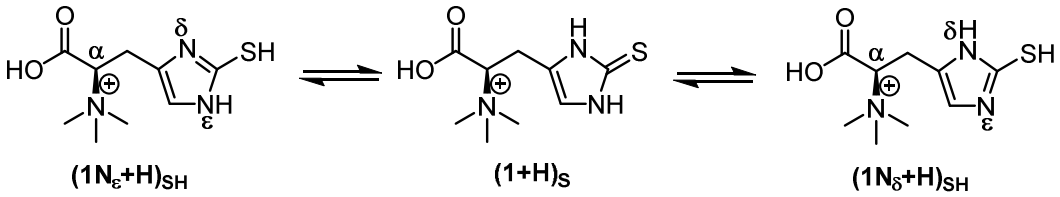
L-ergothioneine (ET) is a sulfur-containing derivative of the amino acid histidine that offers unique antioxidant properties. The enzyme independent redox-chemistry of ET relies on the availability of the thiol tautomer to allow oxidative formation of disulfide bridges, *i.e.*, the tautomeric equilibrium. To study the intrinsic properties of ET the tautomeric equilibrium is studied in the gas-phase by infrared multiphoton dissociation (IRMPD) spectroscopy. The IR ion spectra of isolated molecular ions of ET and of the biosynthetic precursors of ET, *i.e.,* hercynine and N_ε-methyl-hercynine are acquired. The analyte structures are independently investigated by density functional theory (DFT) and computed linear IR-spectra of tautomer ion structures are compared with the gas-phase spectra for identification. For the molecular ion of ET the simulated IR spectra of thione and thiol structures match the recorded IRMPD spectrum and that prevents an individual structure assignment. On the other hand, theory suggests that ET adopts a thione tautomer in MeOH solution which could be carried over from the condensed phase to gas phase and could be kinetically trapped after effective electrospray phase transfer and desolvation. Such a non-thermal behavior is also found for the molecular ions of protonated hercynine and N_ε-methyl-hercynine.
Contrary to that, the sodium complex ions of ET, hercynine and N_ε-methyl-hercynine adopt the respective ground structures predicted by theory, which are reliably identified spectroscopically. For ET the thione tautomer is by far the most stable isomer in the sodium complex molecular ion.

Introduction

L-Ergothioneine (ET) (2-Mercaptohistidine trimethylbetaine) is the trimethylbetaine of L-histidine with a tautomeric thiol/thione group at C-2 of the imidazole ring, which was discovered a century ago in the rye ergot (Scheme 1).(1) Since its initial identification only a few more ET analogs have been isolated from plants and fungi.(2-4) ET is produced by cyanobacteria, mycobacteria and non-yeast like fungi from L-histidine, which is *N*-methylated to yield the trimethylbetaine derivative of histidine, called hercynine, which in turn is enzymatically transformed into ET through the incorporation of sulfur.(5-11) Humans and other vertebrates, even plants, are unable to synthesize ET and are therefore depending on ET uptake from dietary sources, *e.g.* from mushrooms.(12, 13) Once inside mammals, ET is very stable: in rat liver the extrapolated half-life is 1 month; in erythrocytes, the ET content declines only slowly with cell age.(14, 15) High ET concentrations (up to 1 mM) are found only in those cells that express at the plasma membrane a highly-conserved transport protein (ETT, gene symbol *SLC22A4*) for effective and specific ET uptake.(16, 17) The precise physiological role of ET in humans is still not clearly established. However, a large body of evidence suggests that ET is an important cellular antioxidant, given that ET is present in particular in human blood cells, bone marrow, and the lens of the eye, invariably tissues and cells requiring effective protection against oxidative stress.(12, 18-20) Recently, it has been proposed that the unique function of ET may be to scavenge singlet oxygen.(21) Altogether, ET can be considered as a potential vitamin.

In neutral aqueous solution as well as in cellular media at physiological pH the tautomeric equilibrium between the thione and thiol isomers of ET clearly favors the former (Scheme 1).(22) The prevalence of the thione tautomer was confirmed by a X-ray crystal structure of ET dihydrate. Here, the S-C bond length was 1.69 Å, a value typical for thiourea, intermediate between the S-C single (1.82 Å) and double bond lengths (1.56 Å).(23)

The fact that ET adopts predominantly the thione tautomer explains the remarkable resistance to auto-oxidation, which sets ET apart from the other major water-soluble cellular thiol glutathione, which is rapidly oxidized at physiological pH.(5, 24) Also unlike glutathione, ET does not deliver hydroxyl radicals in the Fenton reaction from hydrogen peroxide in the presence of Fe^{2+} ions.(25) Most importantly, ET's redox chemistry proceeds non-enzymatically in cellular media. Thus, the antioxidant properties of ET may rely on the availability of the thiol tautomer for the oxidative formation of disulfide bridges, *i.e.*, the tautomeric equilibrium.(20)



Scheme 1. Tautomeric equilibrium of ergothioneine ET (2-Mercapto-L-histidine trimethylbetaine) isomers. The thione tautomer **$(1+H)_S$**, shown here as protonated ET, is the predominant form in aqueous solutions at physiological pH.(22)

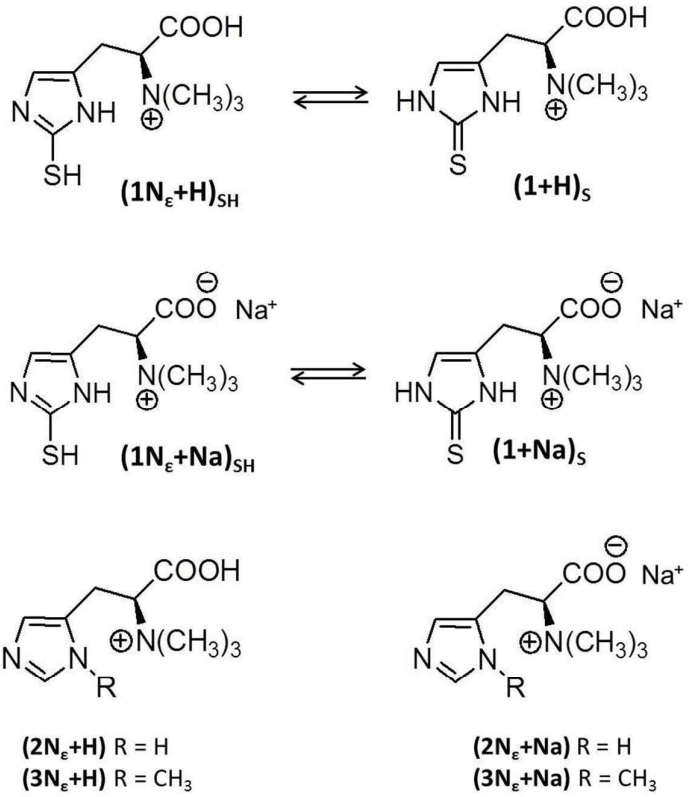
We now aim to study tautomer structures of ET and their intrinsic properties, its biosynthetic precursor hercynine and also of *N*-methyl-hercynine by infrared multiphoton dissociation (IRMPD) spectroscopy and theory. We selected the singly charged molecular ions and the sodium complex ions as analytes for the gas-phase study. These ions are stored in an ion trap MS instrument and the IRMPD spectra should provide fundamental pieces of information on the individual ion structures and thereby also on the tautomeric equilibrium of isolated ET molecular ions.(26-31)

IRMPD spectroscopy is, unlike classical IR spectroscopy, an "action spectroscopy" method, which allows the structure elucidation of ions stored in a trapping device. In IRMPD spectroscopy, a given precursor ion is slowly heated by absorption of numerous IR photons delivered by an appropriate wavelength tunable light source, *e.g.* a free electron laser (FEL).(32-37) Upon intramolecular vibrational redistribution (IVR), the photo-activated ion gets globally heated and eventually can cross the critical energy barriers of one or more fragmentation channels and dissociates.(35, 38) The IRMPD spectra are then acquired by simultaneous recording of the signal intensity of the precursor and product ion(s), as the IR wavelength of the light used for precursor ion activation is tuned (here, between 5-20 μm). Signals appear in the IRMPD spectrum when the precursor ion species is at resonance with the laser radiation and is depleted by IRMPD and product ions are formed. The IRMPD spectra are interpreted in comparison to computed linear IR spectra of candidate structures identified by density functional theory (DFT), allowing structure identification and assignment of individual constitutional isomers, tautomers, and also of conformers. This analytical approach is best suited for the analysis of compounds that differ in their IR active chromophores.(35-37)

Results and Discussion

Molecular ions selected for analysis. The IRMPD spectroscopic investigation of ET includes the protonated betaine molecular cation as well as the sodium complex molecular ion to also probe the influence of an exemplary physiological alkali metal cation such as sodium on the tautomeric equilibrium of ET as Scheme 2 illustrates. The study is complemented by the

analysis of related L-histidine derivative compounds including hercynine and *N*-methyl-hercynine as benchmarks.(39)



Scheme 2. Protonated molecular ions of ET in the thione $\mathbf{(1+H)_S}$ *vs.* the thiol tautomer structure $\mathbf{(1N_\varepsilon+H)_{SH}}$ as well as the tautomeric equilibrium of the sodium complex molecular ions of ET $\mathbf{(1N_\varepsilon+Na)_{SH}}$ and $\mathbf{(1+Na)_S}$, all probed by IRMPD spectroscopy and theory. Protonated and sodium complex molecular ions of hercynine $\mathbf{(2N_\varepsilon+H)}$ & $\mathbf{(2N_\varepsilon+Na)}$ and of $\boldsymbol{N_\varepsilon}$-methyl-hercynine $\mathbf{(3N_\varepsilon+H)}$ & $\mathbf{(3N_\varepsilon+Na)}$ are also included in this study as reference compounds for comparison.

IRMPD spectroscopy and computational analysis of the protonated molecular ions. The computed molecular ions of protonated ET are presented in Figure 1 (structures **a**, **a2, b, c** and **c2**), which exhibit characteristic features differing from the computationally identified structures of the protonated molecular ion structures of L-histidine reported by Armentrout *et al.*(27, 28) In particular, the tri-methyl-betaine moiety of ET is permanently charged and eliminates the Lewis basicity of the *N*-terminus that is instrumental in the ion structures of protonated His. The most stable ion structure of protonated ET, the thiol $\mathbf{(1N_\varepsilon+H)_{SH}}$ molecular ion **b** presented in the second panel of Figure 1, is substantially stabilized by a hydrogen bond COO-H···N interaction of the carboxyl functionality with the N_δ imidazole nitrogen. In contrast to that, the imidazole nitrogen of protonated His is the most basic site and serves as the protonation site in all the molecular ions of L-histidine identified by theory,

additionally stabilized by hydrogen bonding interactions with either the *N*-terminal amine nitrogen or the *C*-terminal carbonyl oxygen.(27, 28)

Five critical ion structures are identified by theory for the protonated molecular ions of ET, *i.e.* three similarly stable **$(1N_{\varepsilon}+H)_{SH}$** thiols **b, c** and **c2** (at 0.0 kJ mol^{-1}, 3.9 kJ mol^{-1} and at 4.8 kJ mol^{-1}) and two thione tautomers **$(1+H)_S$ a** (26.2 kJ mol^{-1}) and **$(1+H)_S$ a2** (27.3 kJ mol^{-1}) as Figure 1 illustrates (see SI for details). Others [such as **$(1N_{\delta}+H)_{SH}$**] were calculated as well, but found to be significantly higher in energy. The computed linear IR spectra of the thione molecular ion **a** and **a2**, which are the least stable of the five structures considered are shown in the top panels of Figure 1, and those of the three thiol **$(1N_{\varepsilon}+H)_{SH}$** conformers **b, c** and **c2** are presented in the panels below.

Figure 1.

Figure 1. Calculated IR spectra of five low-energy tautomers of ET are compared with the IRMPD-spectrum of the protonated molecular ion of ET at *m/z* 230 (black trace). The computed spectra of a **$(1+H)_S$** thione structures **a** and **a2** and three **$(1N_{\varepsilon}+H)_{SH}$** thiol structures **b**, **c** and **c2** are considered (compare Scheme 2). The thione tautomer **a2** is found to be the most stable structure in methanol solution (compare Figure 2). All band origins of the computed ET ions are presented in Table S1 in the Supporting Information (SI).

The IR spectra of the thione tautomers **a** and **a2**, shown in Figure 1, are dominated by a very strong stretching mode of the C=S moiety around 1462 cm^{-1}, a combination band mainly originating from the O-H in-plane bending mode at 1140 cm^{-1} and the asymmetric carbonyl stretching mode $\nu_{C=O}$ of the C-terminus at 1767 cm^{-1}. All band origins of the computed ET ions are presented in Table S1 in the Supporting Information (SI). Although the computed spectra are in good general agreement with the IRMPD signals with respect to band position, the intensity of the former two absorptions is predicted to be much stronger than actually found in the IRMPD spectrum (black trace).

The computed IR spectrum of **$(1N_{\varepsilon}+H)_{SH}$** thiol conformer **c** is an overall convincing match of the recorded spectrum concerning band positions and signal intensities suggesting the predominant presence of this isomer in the gas phase. All significant bands found experimentally meet computed counterparts as shown in the third panel of Figure 1, although this conformer is slightly less stable (3.9 kJ mol^{-1}) than the ground structure thiol **b**. Especially the vibration at around 1140 cm^{-1} is important as the O-H in-plane bending mode of the thiol conformer **c** is resonant there.(27, 31) The thiol structure **b** (0.0 kJ mol^{-1}) is additionally stabilized by a strong hydrogen bond between the imidazole N_{δ} nitrogen and the C-terminal OH. Consequently, the O-H in-plane bending mode of this thiol tautomer is significantly blue shifted to 1480 cm^{-1} explaining the absence of any absorption in the computed IR spectrum around 1140 cm^{-1} (Table S1 in the SI). Apart from this, the spectrum of thiol **b** is consistent with the recorded IRMPD spectrum. For further clarification also the wavenumber region between 3300 and 3600 cm^{-1} was probed (see Figure 1). Here, two bands can be observed in the experimental spectrum at 3490 cm^{-1} and 3550 cm^{-1}, which

match the theoretical predictions for OH and NH stretching modes of the thione **a** and the thiols **c** and **c2**. However, thiol **b** exhibits only the NH stretching mode in this region, while the carboxylate is shifted due to the strong hydrogen bond interaction (see Figure 1). This indicates that structure **b**, although being the lowest energy structure, is not the dominant tautomer or may not be present at all. Hence, the qualitative inspection of the IRMPD spectra and the comparison with computed data sets suggests a non-thermal distribution of ion structures with an important high contribution of either conformer **c** or **c2** than could be expected based on the operating temperature of the trap.

To investigate this further we probed the relevant isomers of ET in MeOH, the spray solvent used for the ESI-MS experiments (see experimental part on theory and the SI), to probe whether a solution-phase favored ion structure of ET was transferred to the gas phase, where the isomerization to the thermodynamic minimum of the gas phase environment is kinetically hindered.(40-42) Such a carry-over phenomenon was already found for deprotonated bifunctional acids like 4-hydroxybenzoic acid, 6-hydroxynicotinic acid and trans-para-coumaric acid and was reliably evidenced by IRMPD spectroscopy.(40-42) Our calculations suggest that the molecular ions of ET predominantly adopt thione tautomer structure **a2** in a polar methanol solution (see Figures 1 and 2). In the gas phase this structure is 1.1 kJ mol^{-1} less stable than isomer **a** as indicated in Figure 1. However, in MeOH it is 5.5 kJ mol^{-1} more stable. Moreover, our calculations show that the thiol isomers **b** and **c** of protonated ET are less stable by 19.9 and 33.3 kJ mol^{-1} in MeOH, respectively; a result that is in line with the behavior of ET in physiological solutions.(22) In addition, we note that *e.g.* the zwitter-ionic form of **a2** is less stable than **a2** by 33.5 kJ mol^{-1}. Even more so, the energy profile and the mechanistic pathway presented in Figure 2 suggest that the conversion from the thione tautomer of ET present in the methanol solution to an intermediate thiol is kinetically inhibited and the subsequent formation of isomer **b** is hindered. In detail, the process for interconversion from the thione **a2** into isomer **b** involves the hydrogen transfer from N_δ to S. In MeOH the free energy barrier height was found to be 167.2 kJ mol^{-1}, whereas in the gas phase this decreased to 136.2 kJ mol^{-1} (energy barrier height: 136.8 kJ mol^{-1}). Given that there is no thermodynamic driver for the isomerization in MeOH, this isomerization can only take place when the molecule is already largely or completely desolvated. The process *in vacuo* has an exergonicity of 5.5 kJ mol^{-1}. The subsequent isomerization into isomer **b** has a comparatively lower barrier of 19.3 kJ mol^{-1} compared to the intermediate thiol. Therefore, the effective free energy barrier for the conversion of isomer **a2** into isomer **b** is 136.2 kJ mol^{-1}. Thus, our calculations suggest that the main isomer in the gas phase of ET is not **b** or **c**/**c2**, but **a** or **a2**.

Figure 2.

Figure 2. Free energy profile for the formation of thiol isomer **b** from thione isomer **a2** in the gas phase.

In a recent work, we investigated the hydrogen transfer in a hydroxy-carbene analyte and a free energy barrier of 128.1 kJ mol^{-1} was found for that process.(43) The barrier for

isomerization in the current case here is even higher, suggesting that a non-thermal distribution of molecules in the gas-phase, consisting largely of thione **a2**, is formed and survives for the duration of our experiment. It needs to be noted that the computational IR spectrum of **a** and **a2** are largely indistinguishable as Figure 1 documents, so that we cannot distinguish between the two isomers based on the IRMPD data.

In conclusion, the spectroscopic evidence collected in the gas-phase allows a profound exclusion of the most stable thiol tautomer of ET (thiol **b**), which is confirmed by the computational analysis of the isolated ion structures in the gas phase. On the other hand, theory suggests that ET adopts a thione tautomer in MeOH solution which could be carried over from the condensed phase to gas phase and could be kinetically trapped after effective electrospray phase transfer and desolvation. The computational analysis of the isomerization mechanism as well as the fact that the simulated IR spectra of both the thione structures **a** and **a2** and those of the thiol structures **c** and **c2** match the recorded IRMPD spectrum prevents an individual structure assignment (Figure 1).

In Figure 3 the spectroscopic data set of the protonated hercynine and in Figure 4 the respective spectra of the protonated N_{ε}-Methyl-hercynine molecular ions are presented in comparison to the computed IR spectra of three most prominent ion structures of the respective analytes identified by theory. Similar to the protonated ET case (Figure 1), the ground structures of both the protonated hercynine (lowermost panel in Figure 3) and of the protonated N_{ε}-Methyl-hercynine (lowermost panel in Figure 4) molecular ions are stabilized by a significant hydrogen bonding interaction between the imidazole N_{δ} nitrogen and the C-terminal OH leading to the characteristic blue-shifted O-H in plane bending mode and the absence of an absorption around 1140 cm^{-1} in their computed IR spectra. Clearly, this band is not reproduced in the experimental IR spectra, although otherwise the computed IR spectra of the respective ground structures (lowermost panels in Figures 3 and 4) match all other signals of the respective IRMPD spectra very well. Surprisingly, in this case optimizing the structures of protonated hercynine in MeOH gives the same energy ordering for these conformers. However, in MeOH the lowest energy conformer **c** is more stable by 20.1 kJ mol^{-1} compared to 5.2 kJ mol^{-1} in the gas phase. The absence of significant absorption features in the computed spectrum of conformer **c** at 1140 cm^{-1} in comparison with the recorded spectrum (black trace) and the spectra of conformers **a** and **b** (first and second panel in Figure 3), strongly indicates that conformer **a** and/or **b** dominate, or at least that these two conformers are present besides conformer **c** (lowermost panel in Figure 3). Thus, we investigated this further by including a partial solvation shell in our calculations to introduce the hydrogen bonding that is not present in a PCM calculation. The result of these calculations, which add two methanol molecules hydrogen-bonded to the carboxylic acid group are given in Figure 5. From these calculations it is clear that hydrogen-bonding has a significant effect on the relative energy-ordering of these conformers. It is clear that the 2 methanol complexes based on gas-phase conformer **c** are now the highest in energy. Moreover, for the isomers based on conformers **a** and **b** there is still the possibility of hydrogen-bonding of additional methanol solvent molecules to the imidazole nitrogen, whereas for both methanol complexes based on conformer **c** this is not an option. As a consequence, we

conclude that in solution conformers **a** and/or **b** prevail, leading to their dominance in the gas phase as well and the absence of conformer **c**.

Figure 3.

Figure 3. Calculated IR spectra of three low-energy conformers of protonated hercynine **(2N$_\varepsilon$+H)** are compared to the IRMPD spectrum of the molecular ion of hercynine at *m/z* 198 (black trace). All band origins of the computed conformer ions of protonated hercynine molecular ions are presented in Table S2 in the Supporting Information.

By analogy, it is assumed that protonated N_ε-methyl-hercynine behaves similarly as Figure 4 illustrates. The significant hydrogen-bonding for conformers **a** and **b** in the solution phase leads to them being solely present in the gas phase, whereas the most stable conformer for the gas phase (conformer **c**) consequently will be absent (compare Figures 4 and 5). All band origins of the computed molecular ions of protonated hercynine (Table S2) and of N_ε-methyl-hercynine (Table S3) are presented in the Supporting Information.

Figure 4.

Figure 4. Calculated IR spectra of three low-energy conformers **(3N$_\varepsilon$+H)** of protonated N_ε-methyl-hercynine are compared to the IRMPD spectrum of the molecular ion of hercynine at *m/z* 212 (black trace). All band origins of the computed conformer ions of protonated N_ε-methyl-hercynine are presented in Table S3 in the Supporting Information.

Figure 5.

Figure 5. Four simulated partial solvation shells for hercynine. Panels (a)-(d) are energy-ordered and based on the bare structures of conformers **a**, **b**, and **c** from Figure 3, respectively. The Gibbs energies of the structures in panels (b), (c), and (d) relative to the Gibbs energy of (a) are 1.7 kJ mol^{-1}, 10.1 kJ mol^{-1}, and 12.3 kJ mol^{-1}, respectively.

IRMPD spectroscopy and computational analysis of the sodium complex molecular ions. In Figure 6 the IRMPD spectroscopic results of the sodium complex molecular ion of ET (black trace) are presented in comparison with the computed spectra of the three most competitive ion structures identified by the DFT computations. In the upper panel the energetically disfavored thiol **(1N$_\varepsilon$+Na)$_{SH}$** tautomer **a** at 42.8 kJ mol^{-1} is shown in which the sodium cation is bound to a single carboxylate oxygen of the deprotonated *C*-terminus and the imidazole nitrogen.

Figure 6. Calculated IR spectra of three competitive tautomers of the ET sodium complex molecular ions are compared to the IRMPD spectra of the molecular ion of ET at *m/z* 252 acquired either in the QIT (black trace), or in the FT-ICR (orange trace), which was only acquired from 1000 – 1800 cm^{-1}. The two ET thiols **(1N$_\varepsilon$+Na)$_{SH}$ a** and **b** are found to be less

stable than the ET thione **(1+Na)$_S$ c**. All band origins of the computed ET sodium complex are presented in Table S4 in the Supporting Information.

The inspection of its computed IR spectrum in comparison with the IRMPD spectrum of the ET sodium complex excludes the presence of this ion structure underpinned by the significantly blue shifted asymmetric carbonyl stretching mode $\nu_{C=O}$ of the deprotonated *C*-terminus, which is clearly not matching the experimental band in the spectrum at 1645 cm^{-1}. Moreover, the strong absorption around 1483 cm^{-1} is clearly not observed in the spectrum of this thiol tautomer. In the middle panel of Figure 6 the IR spectrum of the thiol **(1N$_\varepsilon$+Na)$_{SH}$** ion structure **b** at 19 kJ mol^{-1} is compared with the IRMPD spectrum. In this case a much better agreement of the carbonyl vibration $\nu_{C=O}$ with the strong absorption at 1645 cm^{-1} is found as the sodium ion is coordinated to both oxygens of the carboxylate moiety and to the imidazole nitrogen similarly as in the **(1+Na)$_S$** thione structure **c**, which is by far the most stable tautomer of the ET sodium complex in the gas phase (0.0 kJ mol^{-1}). The computed IR spectrum of thione **c** is compared with the IRMPD spectrum in the third panel of Figure 6. The special interaction of the sodium with the nucleophilic sulfur of the thione moiety is remarkable and seems to be decisive for the elevated stability of this tautomer. Besides the match of the *C*-terminal carbonyl vibration $\nu_{C=O}$, related to the shared interaction of both carboxyl oxygens with the sodium, the other prominent band in the IRMPD spectrum around 1480 cm^{-1} is also represented in the IR spectrum of this tautomer, albeit with exaggerated intensity. The symmetric C=S stretching vibration of the thione tautomer **c** is resonant at this photon energy making an identification of this tautomer, which is the clear ground structure in the gas phase, possible. Additionally, the spectrum of thione **c** is also a convincing match of the weak bands around 1100 cm^{-1}, of the well resolved two bands at around 1350 cm^{-1}, observed in the IRMPD spectrum acquired with the FT-ICR instrument (see orange trace in Figure 6 and Table S4, SI), and in the wavenumber range below 1000 cm^{-1}, which further secures the assignment of the thione structure **c**.

In conclusion it is reasonable to assume that thiol **a** is very likely not present in the gas phase on the basis of the mismatching carbonyl fingerprint vibration, but the presence of **(1N$_\varepsilon$+Na)$_{SH}$** thiol **b** cannot be excluded. In this case the carbonyl stretching vibration $\nu_{C=O}$ at 1645 cm^{-1} matches the computational predictions, while the C=S stretching mode around 1480 cm^{-1} is weaker than in the experimental spectrum and doesn't agree as good as the IR spectrum of thione **c**. Therefore, similar to the investigation on the protonated molecular ion of ET, we also computed the ET sodium complex in methanol (see experimental part on theory & SI) to further investigate whether the gas-phase favoured thione **(1+Na)$_S$** ion structure **c** is also favoured in the methanol solution. Our calculations show clearly that the thione **(1+Na)$_S$** ion structure **c** is also favoured in the methanol solution (within the constraints of the PCM model). In this case, tautomer **c** is more stable than tautomer **a** (by 39.7 kJ mol^{-1}) and tautomer **b** (by 43.1 kJ mol^{-1}). Therefore, we conclude that for the ergothioneine sodium complex the thione tautomer is solely present both in solution and in the gas-phase.

Additionally, in Figure 7 the spectroscopic data set of the sodium complex ion of hercynine and in Figure 8 the spectra of the respective N_ε-Methyl-hercynine molecular ions are shown in comparison with the computed IR spectra of three most prominent ion structures of the respective analytes identified by theory. As shown in Figure 6 for the ET sodium complex ion the identification of the respective ground structure of the two sodium complex molecular ions is here also confidently possible. For the sodium complex of hercynine (Figure 7) as well as for the one of N_ε-Methyl-hercynine (Figure 8), the identification of an individual ion structure is possible because the asymmetric carbonyl stretching mode $\nu_{C=O}$ of the deprotonated *C*-terminus appears significantly shifted in the two less stable ion structures. Conformer **a** of the hercynine sodium complex molecular ion (upper panel in Figure 7), as well as conformer **a** of the N_ε-Methyl-hercynine sodium complex (upper panel in Figure 8) both show a significant blue shift of the carbonyl stretching vibration due to the complexation of the sodium cation between the imidazole and an oxygen of the carboxylate moiety ultimately leading to a strengthened C=O double bond of the unbound carbonyl (similar to the thiol $\mathbf{(1N_\varepsilon+Na)_{SH}}$ ion structure **a** of the ET sodium complex molecular ion shown in the upper panel in Figure 6). Contrary to that finding is the red-shifted carbonyl stretching mode $\nu_{C=O}$ of conformers **b** (second panels in Figures 7 and 8) of both reference complex ions in which the sodium is solely ligated to the deprotonated carboxylate moiety and therefore weakening the C=O bond.(27, 28) The most stable molecular ion of these tri-methyl-betaine derivatives of His shows the Lewis-acidic sodium cation bound to the imidazole nitrogen and both oxygens of the deprotonated *C*-terminus, a complexation motif also found for sodiated histidine, where it is however less favored.(28)

Figure 7.

Figure 7. Calculated IR spectra of three low-energy conformers of hercynine sodium complex molecular ions **$\mathbf{(2N_\varepsilon+Na)}$** are compared to the IRMPD spectrum of the molecular ion at *m/z* 220 (black trace). All band origins of the hercynine sodium complex molecular ions **$\mathbf{(2N_\varepsilon+Na)}$** are presented in Table S5 in the Supporting Information.

Figure 8.

Figure 8. Calculated IR spectra of three low-energy **$\mathbf{(3N_\varepsilon+Na)}$** conformers of N_ε-Methyl-hercynine sodium complex molecular ions are compared to the IRMPD spectrum of the molecular ion at *m/z* 234 (black trace). The band origins of the N_ε-Methyl-hercynine sodium complex molecular ions are presented in Table S6 in the Supporting Information.

Conclusions

The tautomeric equilibrium of ET and of two additional histidine derivatives is examined in the gas phase by IRMPD spectroscopy and extensive DFT computations. The experimental data set clearly shows that all three betaine analytes, *i.e.,* the protonated molecular ions of ET, hercynine and N_ε-methyl-hercynine do not adopt the ground state ion structure identified by theory for the gas phase. Extensive computational analysis of the individual ion

structures as well as the isomerization pathways between individual tautomers and conformers suggest that a thione tautomer of ET, which is prevalent in methanolic solution, is kinetically trapped upon desolvation, which in turn offers an explanation for the non-thermal behavior found spectroscopically. This remarkable result is not observed for the set of sodium complex molecular ions, for which a confident identification of the respective gas-phase ground structures is possible. In particular, the sodium complex ion of ET adopts a thione tautomer structure, which is the by far the most stable isomer of this complex molecular ion. This study demonstrates that the ion structures of ET can be successfully investigated in detail by ion spectroscopy and mass spectrometry in the gas phase. Our results evidence the prevalence of the thione tautomer of ET in polar/protic solvents such as methanol and confirm the limited availability of the respective thiol tautomer in such condensed phases. This finding might also help to better understand the anti-oxidant properties of ET at physiological pH in cellular medium.

Experimental

Theory / Computations:

Density functional theory (DFT) calculations were performed using Gaussian09, version D.01.(44) Gaussian was compiled with Gaussian-supplied versions of BLAS and ATLAS.(45, 46) The B3LYP functional was used throughout with the GD3-BJ correction to account for dispersion interactions, whereby it is noted that in this case this correction did not change the answers significantly compared to the bare B3LYP functional.(47, 48) The cc-pVTZ basis set(49, 50) was used throughout with the ultrafine setting for the integrals. All of the structures were fully optimized without any symmetry restrictions. Transition states were located using the QST3 algorithm.(51) Tautomers **a**, **b**, and **c** of ET were also investigated using the w-B97-XD functional. Qualitatively similar results were obtained for this functional (see SI).(52) Frequency calculations in the harmonic approximation were carried out to characterize all stationary points obtained to confirm them as either local minima or transition states. Frequencies were used to calculate free energies in the standard way. All minimum energy structures were identified through the absence of imaginary frequencies. Transition states were identified through the presence of a single imaginary frequency.

This computational procedure was found to give good correlation with experiment in previous work.(43) All (except where specified differently) calculations performed on these systems were done *in vacuo*. For the modelling of the conformers of ergothionine in MeOH the polarizably continuum model (PCM) was used as implemented in Gaussian with the standard parameters for MeOH. Frequencies were scaled by 0.97 in the region between 500 and 1900 cm^{-1}. A scaling factor of 0.957 was used in the O-H stretch region between 3300-3600 cm^{-1} to account for the overestimation of computed frequencies.(53-55) The computed absorptions were broadened by a Gaussian with a FWHM of 12 cm^{-1} to facilitate comparison with experiment.(53-55) For facilitated comparison between computed IR spectra and the

experimental data sets the carbonyl stretching mode was used as the standard benchmark. Any energy differences quoted throughout the study are differences in calculated Gibbs Energies.
The supporting information was created using in-house developed software based on the OpenEye toolkit.(56, 57)

Mass Spectrometry:

Synthesis of hercynine and *N*-Me-hercynine

L-Histidine was purchased from Acros Chemicals, methylionine from Sigma Aldrich. Methanol was obtained in HPLC grade from Fischer Chemicals. And the used water was deionized. The betaines were synthesized by reacting the amino acid with methyliodine according to a standard procedure.(29) L-Histidine (155 mg, 1 mmol), methyliodine (1 mL, 16 mmol) and sodium bicarbonate (1 g, 12 mmol) were suspended in 20 mL H_2O/MeOH (v/v 1/1) and stirred for 16 h under exclusion of sunlight. The solvent was evaporated under reduced pressure and the residue was dissolved in equal portions of chloroform and water (each 5 mL). The aqueous layer was separated and treated with 1M HCl until a clear solution was obtained.

For mass spectrometric analysis the samples were diluted in MeOH/H_2O. All (+)ESI-MS and MS^2 experiments as well as accurate ion mass measurements were conducted on an LTQ-Orbitrap XL instrument (ThermoFisher, Bremen Germany); see Supplementary Figures 1-4 and Table S7. Product ion spectra were acquired in the linear ion trap (LTQ) part of the LTQ-Orbitrap instrument by CID with the He bath gas present ($P = 2 \times 10^{-5}$ Torr) and the product ions were analyzed in the orbitrap. Accurate ion masses were determined in the orbitrap analyser with a resolution of 30000 FWHM with external calibration ($\Delta m < 3$ ppm) or with addition of internal standards ($\Delta m < 2$ ppm). Typical (+)ESI-MS conditions: Flow rate: 5 µLmin^{-1}; Capillary voltage: 3.20 kV; Sheath gas: 4.99 [arb. units]; Aux gas: 2.00 [arb. units]; Resolution: 30000 FWHM.

Ion Spectroscopy

A home-built Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer coupled to the beamline of the Free Electron Laser for Infrared eXperiments (FELIX) was used to record IRMPD spectra in the 500-1900 cm^{-1} range (58-60). Probed ions were formed by electrospray ionization (ESI) using a Micromass Z-spray source from a 1 mM solution of the samples dissolved in MeOH/H2O (v/v 1/1). Ions of interest were mass isolated in the ICR cell, and irradiated with 20 pulses of the FELIX IR laser (energy 10-50 mJ per macropulse of 5 µs duration, bandwidth was around 0.5% of the central frequency). At every frequency step, three mass spectra were summed, and the IRMPD yield was determined (defined as the sum of fragment ion intensities divided by the sum of all ion intensities)(38). An IRMPD spectrum was obtained by plotting the yield as a function of the IR laser frequency. The yield was

linearly corrected for the frequency dependent variation of the IR laser pulse energy. The IRMPD spectrum of the ergothioneine sodium complex molecular ion was also recorded on a modified 3D quadrupole ion trap (QIT) mass spectrometer (Bruker amaZon speed ETD) coupled to the FELIX beamline (61, 62) in order to obtain an improved signal to noise ratio (note that the spectra obtained on both instruments were found to be identical). Here, the solutions used for ESI were 0.1 µM. Finally, the IRMPD spectrum of protonated ergothioneine in the 3400-3600 cm^{-1} region was recorded in the QIT using an optical parametric oscillator/amplifier (OPO/OPA) laser source (LaserVision, 15 mJ per pulse of 5 ns duration, bandwidth 3 cm^{-1}).(61)

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The skillful assistance of the entire FELIX staff is gratefully acknowledged. We gratefully acknowledge the *Nederlandse Organisatie voor Wetenschappelijk Onderzoek* (NWO) for the support of the FELIX Laboratory. A license for the OpenEye tools, obtained via the free academic licensing program, is gratefully acknowledged. Funding from the European Community's Seventh Framework Programme (FP7/2007−2013) under grant agreement no. 312284, is gratefully acknowledged.

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Table of contents entry:

TOC Graphic

Gas-phase analysis of ergothioneine molecular ions allows differentiating thiol from thione tautomer structures

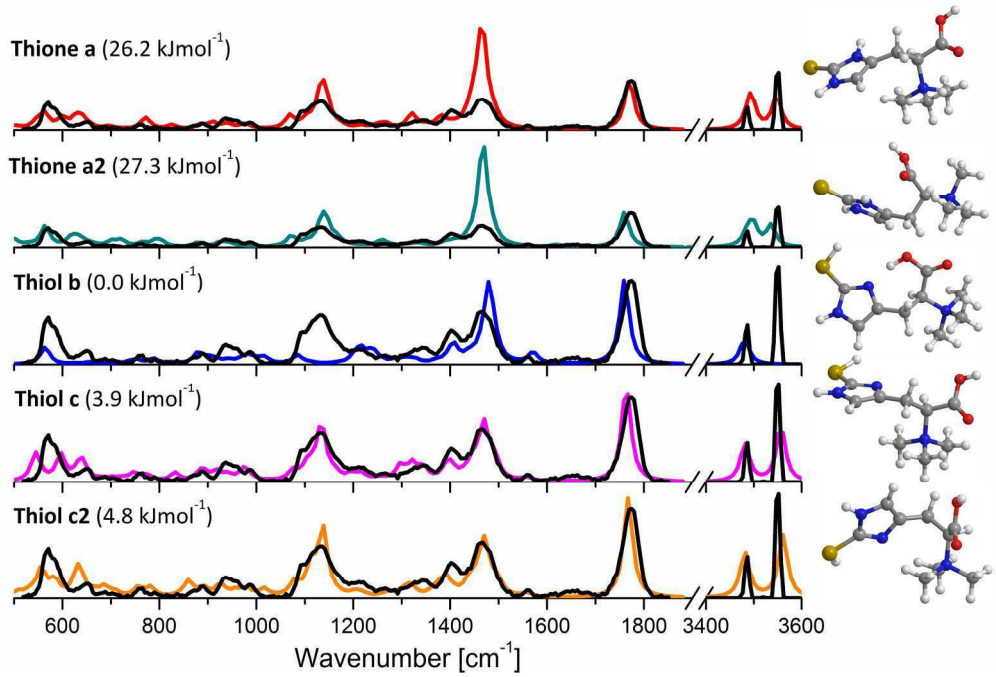

Figure 1. Calculated IR spectra of five low-energy tautomers of ET are compared with the IRMPD-spectrum of the protonated molecular ion of ET at m/z 230 (black trace). The computed spectra of a (1+H)S thione structures a and a2 and three (1Nε+H)SH thiol structures b, c and c2 are considered (compare Scheme 2). The thione tautomer a2 is found to be the most stable structure in methanol solution (compare Figure 2). All band origins of the computed ET ions are presented in Table S1 in the Supporting Information (SI).

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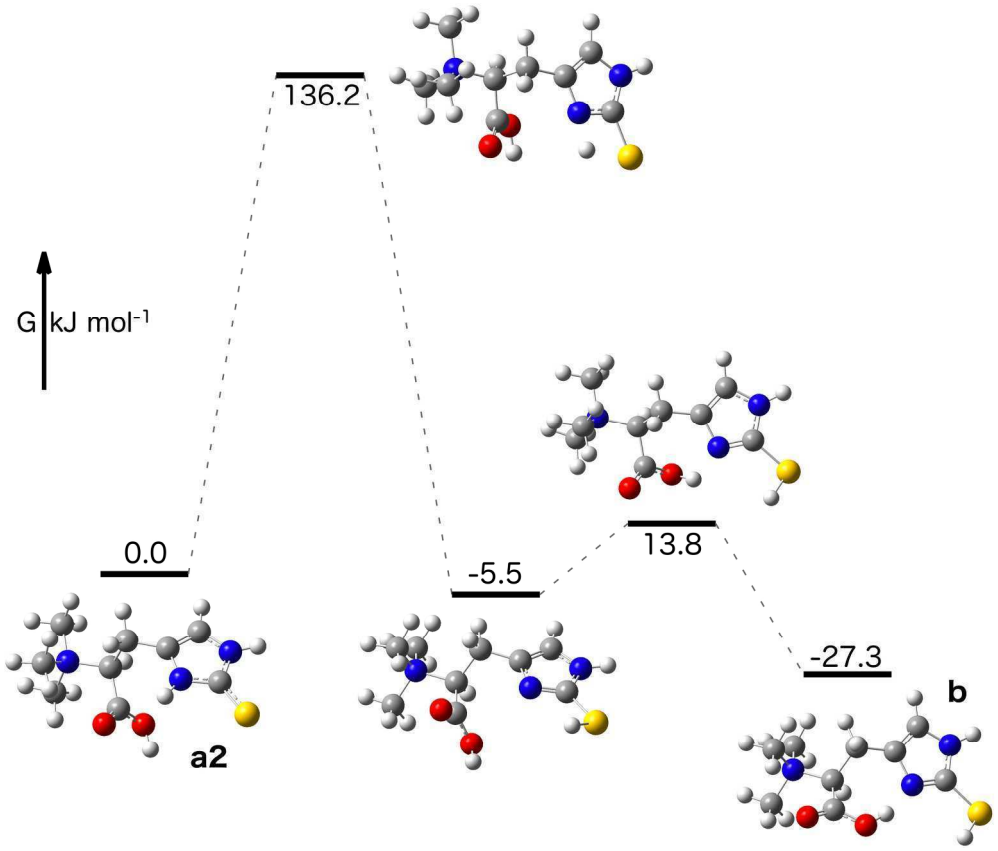

Figure 2. Free energy profile for the formation of thiol isomer b from thione isomer a2 in the gas phase.

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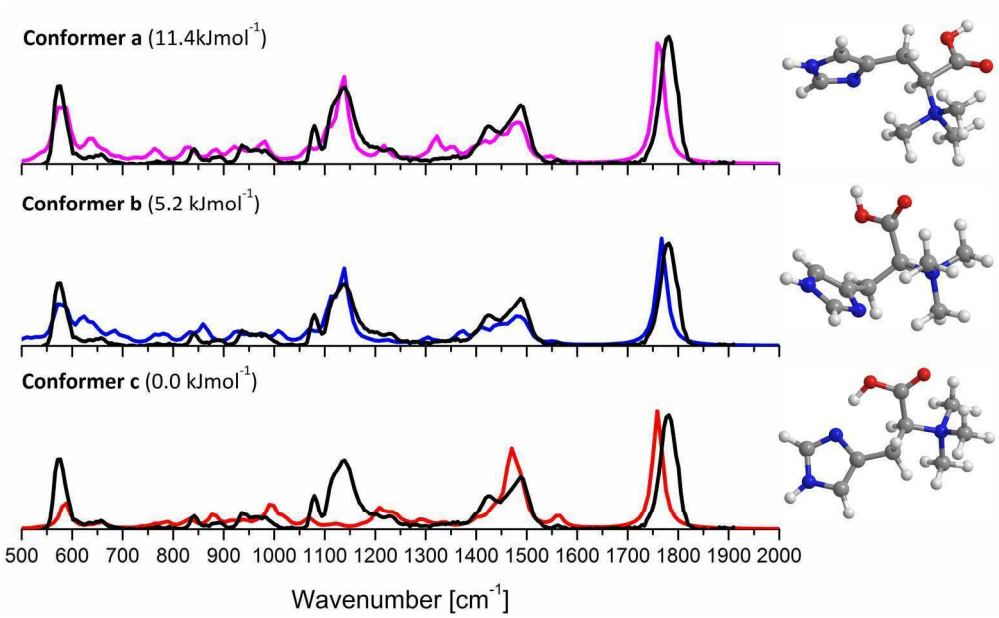

Figure 3. Calculated IR spectra of three low-energy conformers of protonated hercynine (2Nε+H) are compared to the IRMPD spectrum of the molecular ion of hercynine at m/z 198 (black trace). All band origins of the computed conformer ions of protonated hercynine molecular ions are presented in Table S2 in the Supporting Information.

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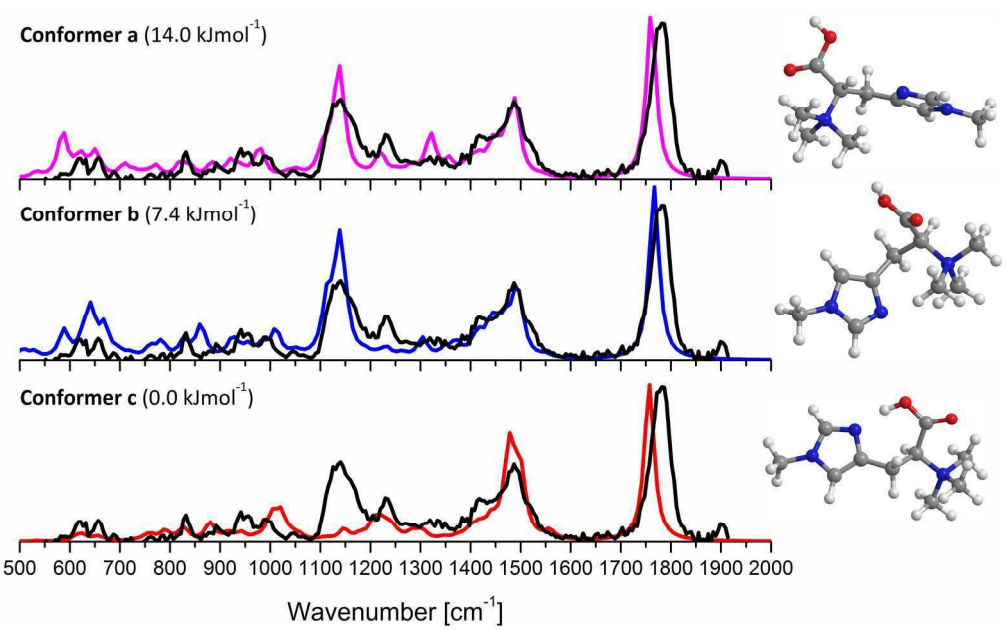

Figure 4. Calculated IR spectra of three low-energy conformers (3Nε+H) of protonated Nε-methyl-hercynine are compared to the IRMPD spectrum of the molecular ion of hercynine at m/z 212 (black trace). All band origins of the computed conformer ions of protonated Nε-methyl-hercynine are presented in Table S3 in the Supporting Information.

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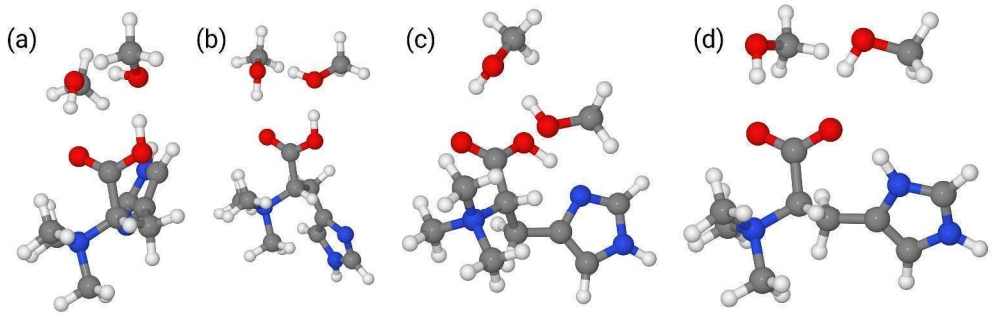

Figure 5. Four simulated partial solvation shells for hercynine. Panels (a)-(d) are energy-ordered and based on the bare structures of conformers a, b, and c from Figure 3, respectively. The Gibbs energies of the structures in panels (b), (c), and (d) relative to the Gibbs energy of (a) are 1.7 kJ mol-1, 10.1 kJ mol-1, and 12.3 kJ mol-1, respectively.

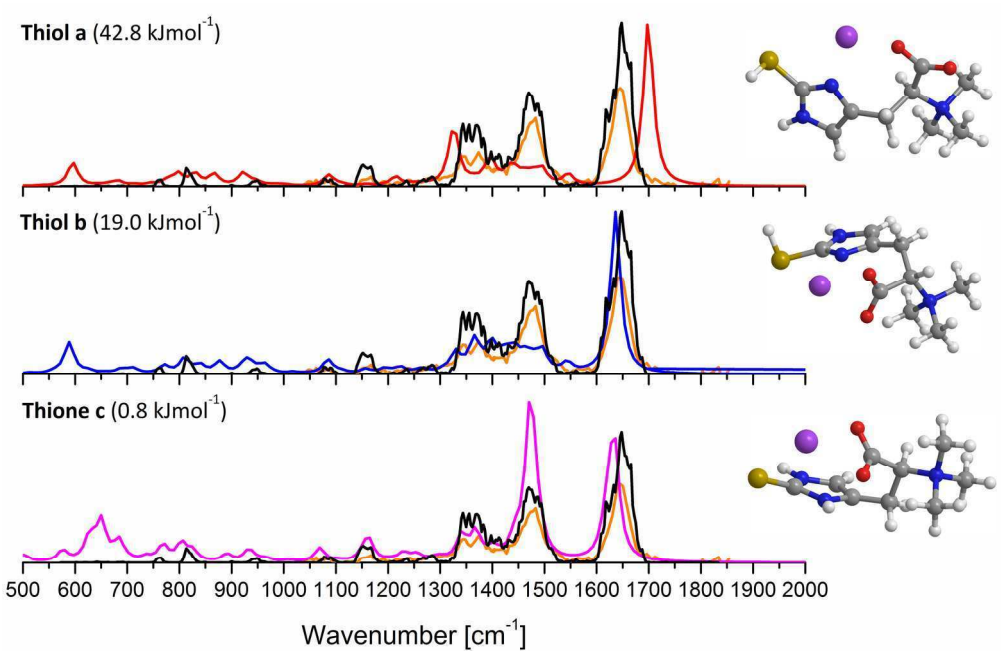

Figure 6. Calculated IR spectra of three competitive tautomers of the ET sodium complex molecular ions are compared to the IRMPD spectra of the molecular ion of ET at m/z 252 acquired either in the QIT (black trace), or in the FT-ICR (orange trace), which was only acquired from 1000 – 1800 cm-1. The two ET thiols (1Nε+Na)SH a and b are found to be less stable than the ET thione (1+Na)S c. All band origins of the computed ET sodium complex are presented in Table S4 in the Supporting Information.

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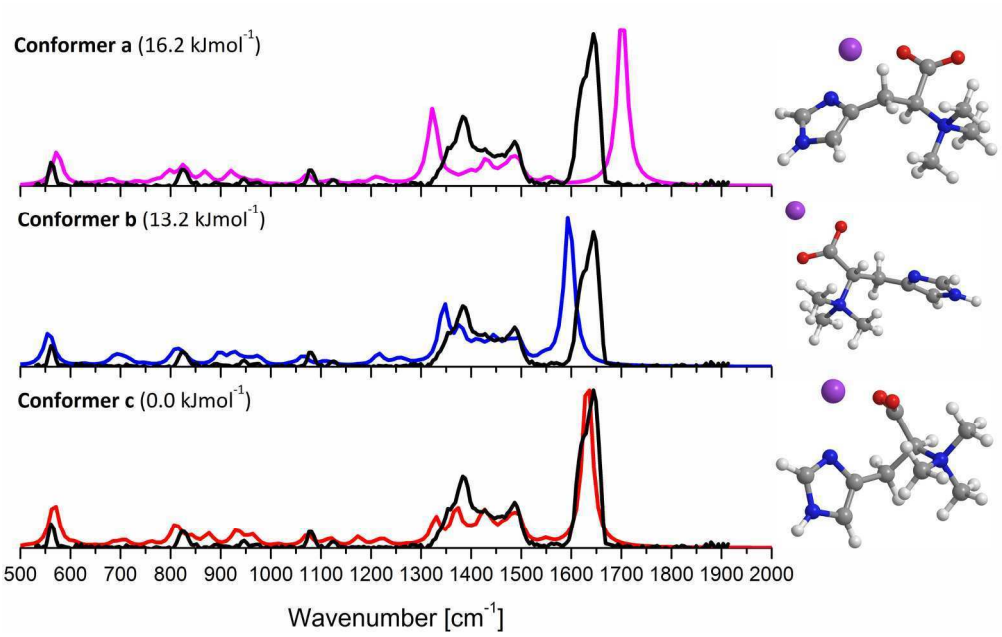

Figure 7. Calculated IR spectra of three low-energy conformers of hercynine sodium complex molecular ions (2Nε+Na) are compared to the IRMPD spectrum of the molecular ion at m/z 220 (black trace). All band origins of the hercynine sodium complex molecular ions (2Nε+Na) are presented in Table S5 in the Supporting Information.

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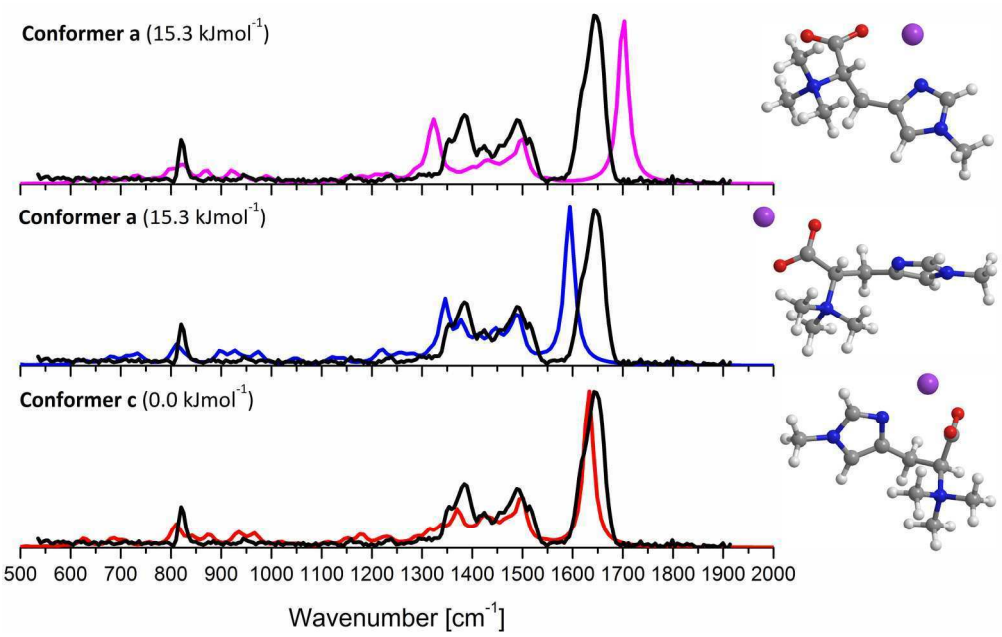

Figure 8. Calculated IR spectra of three low-energy (3Nε+Na) conformers of Nε-Methyl-hercynine sodium complex molecular ions are compared to the IRMPD spectrum of the molecular ion at m/z 234 (black trace). The band origins of the Nε-Methyl-hercynine sodium complex molecular ions are presented in Table S6 in the Supporting Information.

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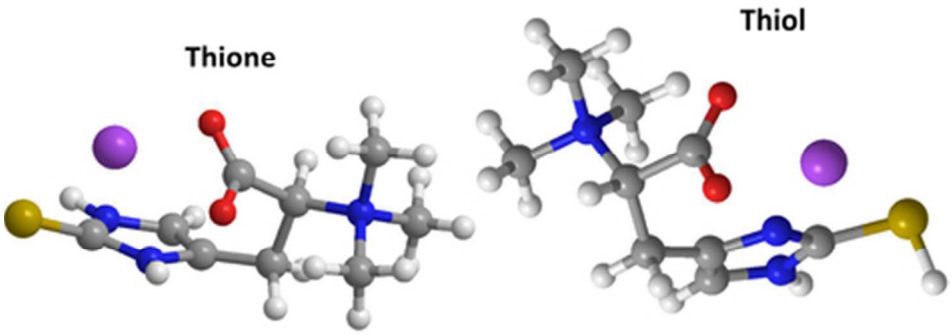

39x19mm (300 x 300 DPI)

Ergothioneine and related Histidine Derivatives in the Gas Phase: Tautomer Structures determined by IRMPD-Spectroscopy and Theory Supplementary Information

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CONTENTS

S1. ADDITIONAL FIGURES

Additional Figures:

Figure S1. (+)ESI-MS of Ergothioneine, MeOH

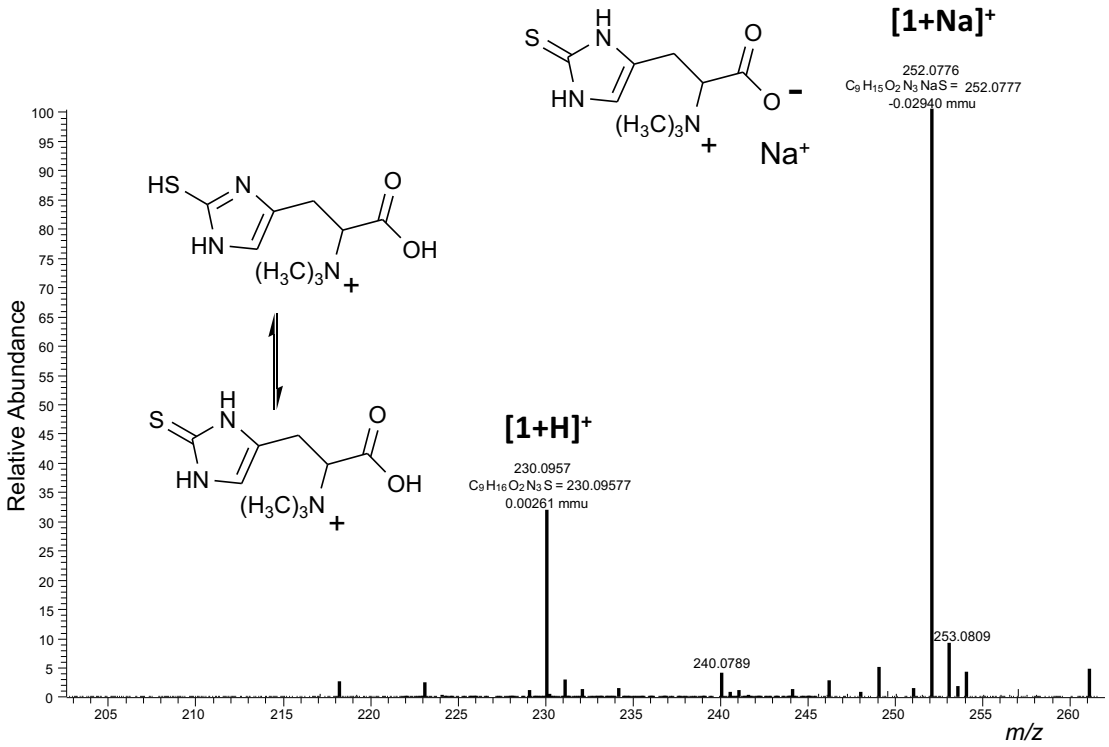


Figure S2. (+)ESI-MS^2 of Ergothioneine **[1+H]$^+$** *m/z* 230

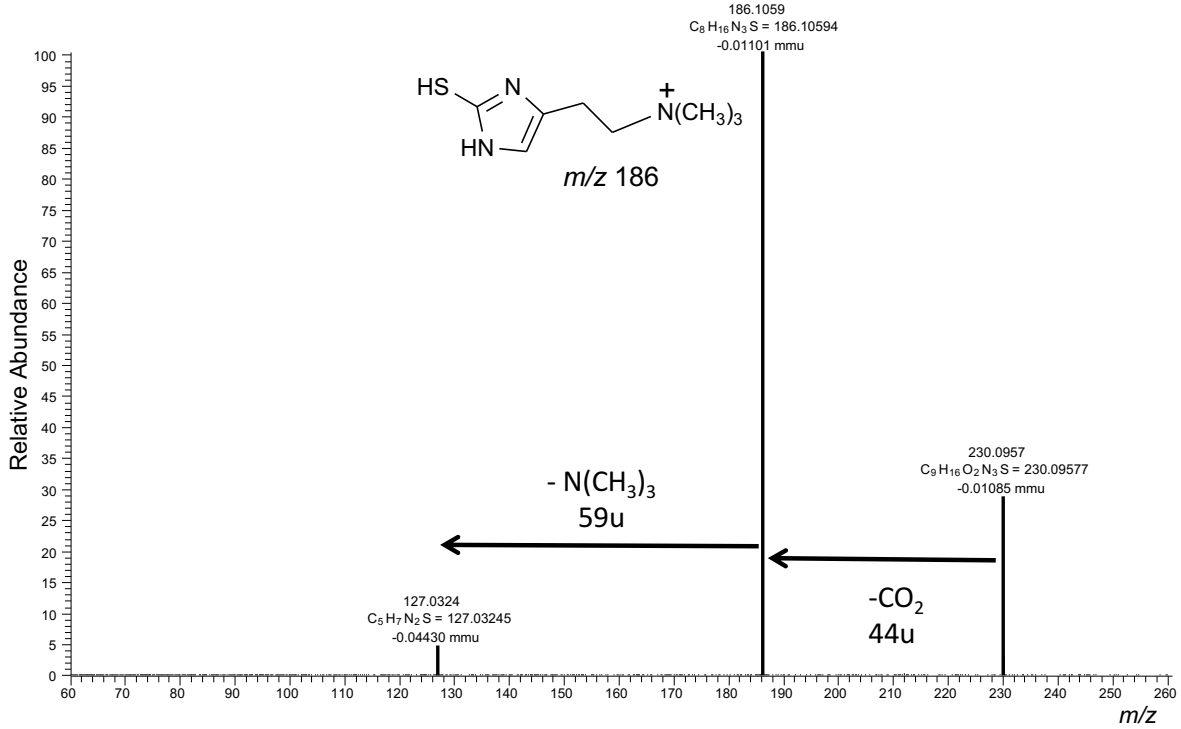


Figure S3. (+)ESI-MS^3 of Ergothioneine **[1+H]$^+$**
m/z 230 → *m/z* 186 →

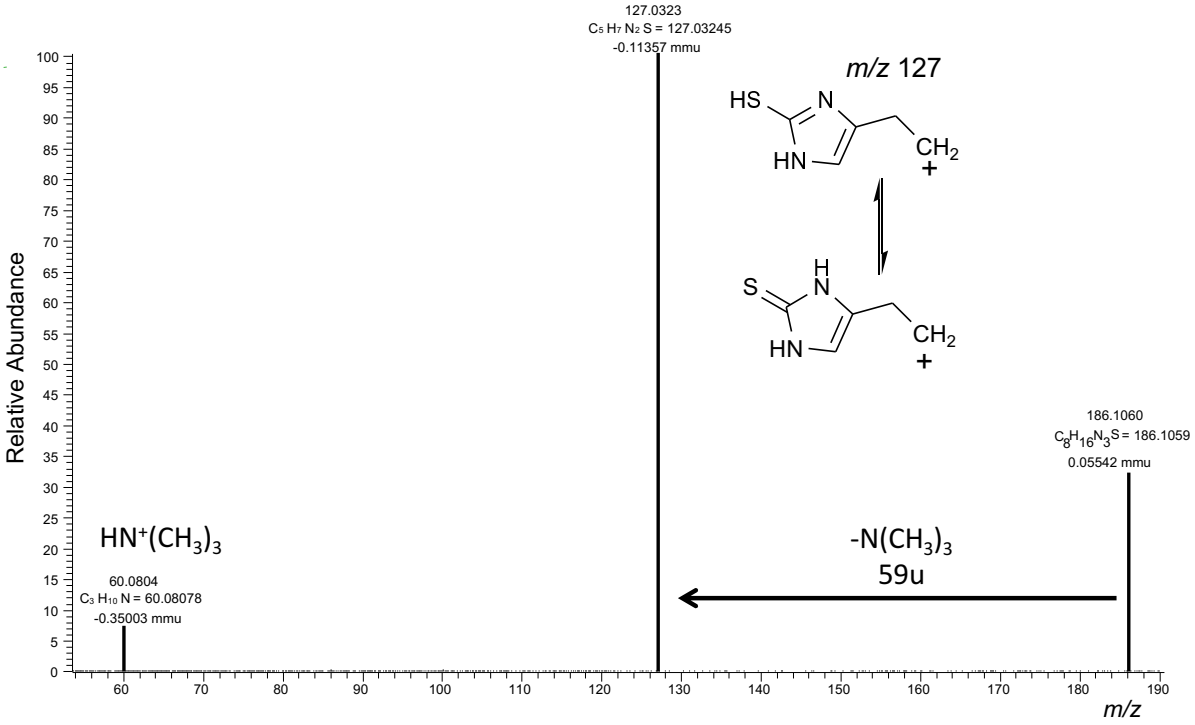
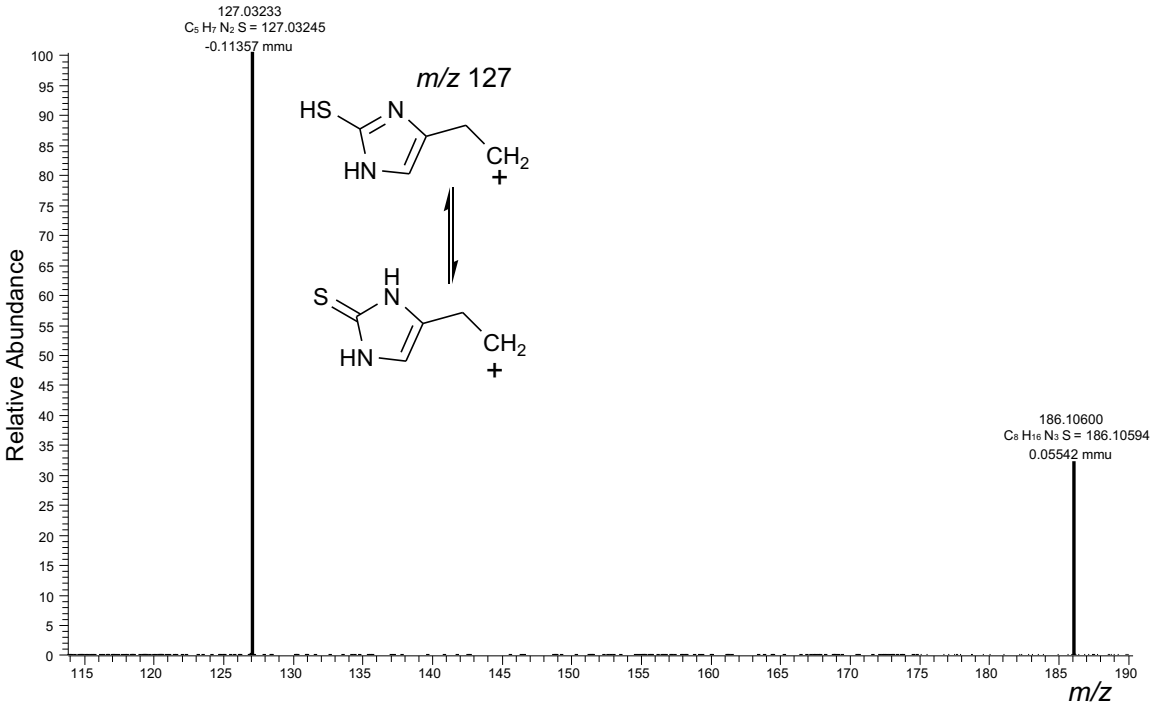


Figure S4. (+)ESI-MS^3 of Ergothioneine **[1+H]**$^+$ *m/z* 230 → *m/z* 186 →



S2. ADDITIONAL TABLES

Table S1: IRMPD spectrum of the protonated molecular ion of ergothioneine and the band origins of the computed ET ions

	Experiment	Theory				
Vibrational Mode		$(1+H)_s$ (a)	$(1N_\varepsilon+H)_{SH}$ (b)	$(1N_\varepsilon+H)_{SH}$ (c)	$(1N_\varepsilon+H)_{SH}$ (c2)	$(1+H)_s$ (a2)
O-H Stretching	3551	3518		3530	3535	3535
N-H Stretching	3487	3467	3458	3458	3458	3501
C=O Stretching	1775	1767	1759	1767	1767	1759
C=C Stretching	1559		1567	1558	1559	
C=S Stretching	1468	1462/1139				1471
N-H Bending in plane Imidazole	1468			1471	1468	1471/1139
Betaine Wagging	1402		1235	1401		1401
C-H Bending in plane		1382/1322				1261
CH_2 Wagging			1271	1340	1319	
O-H Bending in plane	1468	1322/1217/1139	1479	1322/1130	1138	
N-C-N Stretching			1409			
C-N=C-C Stretching				1296		
Combinatoric Wagging	1216			1200		
HC-NH Stretching	1061/1096	1069	1086	1078	1390	1069
CH_2-CH Stretching	962	973				
C-N$(CH_3)_3$ Stretching	962/837	938/825	877	973/830	860	877
N-CH_3 Stretching		912		921		
S-H Bending	871			886		
HN-C-NH						938
HO-C=O Wagging	765			772		
C-H Bending out of plane Imidazole		772		746	756	
HO-C=O Scissoring	648			641		
O-H Bending out of plane	583	598		598	631/687	702
N-H Bending out of plane Imidazole	571	563	563	545	556	562

Table S2: IRMPD spectrum of the protonated molecular ion of hercynine **[2+H]**$^+$ at *m/z* 198 and the band origins of the computed ET ions

	Experiment	Theory		
Vibrational Mode		(2Nε+H) (a)	(2Nε+H) (b)	(2Nε+H) (c)
C=O Stretching + O-H Bending	1781	1759	1767	1759
C=C Stretching		1549	1549	1558
HC=N Stretching + CH_3 Scissoring	1488	1479/1444	1479	
CH_2 Scissoring			1444	
HC-NH Stretching	1423	1418/1069	1409/1069	
HOOCC-H Bending		1322	1374	
O-H Bending			1305	1471
C-H Bending in plane Imidazole	1229	1217	1226	
CH_2 Wagging		1348		1287
CH_3 Wagging		1104		
C-OH Stretching	1139	1139	1139	
Betaine Wagging				1235
CH_3 Torsion			1113	1209
C=N=C Stretching				1069
HC-CH_2 Stretching			1008	
CH_2 Rocking	980	886	973	
N-CH_3 Stretching		921	922	
C-N(CH_3)$_3$ Stretching			859	877
C-H Bending out of plane Imid	842	826	833	833
O-H Bending out of plane			781	990
COOH Scissoring	657	641		659
Imidazole out of plane	576	580	685	589

Table S3: IRMPD spectrum of the protonated molecular ion of protonated N_{ε}-Methyl-hercynine **[3+H]$^+$** at *m/z* 212 and the band origins of the computed ET ions

	Experiment	Theory		
Vibrational Mode		(3Nε+H) (a)	(3Nε+H) (b)	(3Nε+H) (c)
C=O Stretching + O-H Bending	1782	1759	1767	1758
C=C Stretching	1521		1549	1556
N=C Stretching + CH3 Wagging Imidazole	1487	1488	1488	1502
CH_3 Scissoring		1444		1478
HC-COO	1418	1418/886		
CH2 Wagging		1357		1300
Betaine Wagging		536	1444	1214
CH_3 Wagging Imidazole			1418	
HOOCC-H Bending in		1322	1374	
O-H Bending in plane		1278	1305	1020/1005
H Imidazole in plane	1230	1217		
C-OH Stretching		1139		
CH_3 Torsion Imidazole + H_3CN=CH Stretching	1046	1051		
CH_2 Rocking		982		
C-N(CH_3)$_3$ Stretching		921	1261	881
(N=)C-H Bending in plane	1230		1235	826
O-H Bending in plane	1141		1139	
CH_2-CH Stretching			1008	
Imidazole Torsion	991		982	
N-CH_3 Stretching Betaine	952		955	
Betaine Motion			929	
C-N(CH_3)$_3$ Stretching			859	
(N=)C-H Bending out of plane	832		825	
Combinatoric			781	
(C=)C-H Bending out of plane			763	
(C=)C-H Bending in plane				1145
COOH Scissoring	657	650		
O-H Bending out of plane	622	624/589	667/641/589	
Imidazole Bending out of plane		825/711	628	625

Table S4: IRMPD spectrum of the sodiated molecular ion of ergothioneine **[1+Na]**$^+$ at *m/z* 252 and the band origins of the computed ET ions

	Experiment QIT	Experiment FTICR	Theory		
Vibrational Mode			$(1N\varepsilon+Na)_{SH}$ (a)	$(1N\varepsilon+Na)_{SH}$ (b)	$(1+Na)_S$ (c)
COO Asymmetric Stretching	1648	1645	1698	1636	1636
C-S Stretching + N-H Bending in plane	1487/1470	1483			1474/1165
C=C Stretching			1549	1540	
CH_3 Scissoring			1497	1497	
CH_3 Wagging	1430		1436		1401
N-H Bending in plane Imidazole				1444	
HN-C=N Asymmetric Stretching	1374	1373	1392	1401	
CH_2 Wagging + C-COO Stretching	1356/1343	1348		1366	1366
CH_2 Wagging + OOCC-H Bending			1322	1331	
CH_2 Torsion			1217	1270	
C-N$(CH_3)_3$					1252
Betaine Wagging				1226	1235
OOCC-H Bending	1169/1152	1167		1191	1340
HC-NH Stretching	1082		1086	1086	1069
C-N$(CH_3)_3$ Stretching	948/813				937/807
C-H out of plane Bending Imidazole	765				772

Table S5: IRMPD spectrum of the sodiated molecular ion of hercynine **[2+Na]**$^+$ *m/z* 220 and the band origins of the computed ET ions

	Experiment	Theory		
Vibrational Mode		(2Nε+Na) (a)	(2Nε+Na) (b)	(2Nε+Na) (c)
COO Asymmetric Stretching	1644	1698	1593	1636
C=C Stretching	1570	1558	1545	1549
CH_3 Scissoring	1487/1428	1488/1427	1497	1488
CH_3 Torsion			1479/1444/1113	
CH_3 Wagging		1401	1409	
CH_2 Scissoring				1427
HC-COO Stretching	1383	1322	1374	1374
OOCC-H Bending+ CH_2 Wagging			1348	
CH_2 Torsion		1174/676	1261	
CH_2 Wagging				1331
H-C Bending in plane Imidazole + CH_3 Torsion			1217	1226
OOC-CH Stretching + CH_2 Torsion				1174
HC-NH Stretching			1069	1519/1078
HC=NH	1126/1081	1121/1069		
C=N-C Asymmetric Stretching	972	973		
C-$N(CH_3)_3$		868		
CH_2 Rocking	972	825	973/903	964/877
N-CH_3 Stretching		921	929	929/711
CH_2 Rocking + C-COO Stretching				842
(N=)C-H Bending out of plane + C-$N(CH_3)_3$ Stretching				807
COO Scissoring		798		
(C=)C-H Bending out of plane	822	737	816	763
Imidazole Torsion			632	685
HC-CH_2 Stretching				606
Imidazole Bending out of plane	561	571	554	571

Table S6: IRMPD spectrum of the sodiated molecular ion of protonated *N*ε-Methyl-hercynine **[3+Na]**$^+$ at *m/z* 234 and the band origins of the computed ET ions

	Experiment	Theory		
Vibrational Mode		(3Nε+Na) (a)	(3Nε+Na) (b)	(3Nε+Na) (c)
COO Asymmetric Stretching	1642	1703	1595	1633
HC=N Stretching + CH_3 Wagging Imidazole	1514/1489	1502	1486/1408	1494
CH_3 Wagging Betaine		1432/1401		
CH_2 Scissoring	1424			1424
CH Bending + OOCC-H Bending	1384/1354	1323	1377	
OOCC-H Bending		1207		
HC-COO Stretching				1370
H_3CN-CH Stretching				1339
CH_2 Wagging + OOCC-H Bending				1315
CH_2 Torsion			1253	1292
C-H Bending in plane Imidazole	1239		1346	1230
CH_2 Torsion + OOCC-H Bending	1173			1176
(C=)N-C(=N) Stretching	979	989	1284	
(C=)C-H Bending in plane	1158	1152	1145	1152
H Imidazole in plane			1222	
CH_3 Torsion Betaine		803	1447/1121	1114
CH_3 Torsion Imidazole			1051	178
CH_2-CH Stretching				1020
N-CH_3 Stretching Betaine		920		
Imidazole Stretching				966
Betaine Motion/Combined Deformation	944			935
CH_2 Rocking		1176	896	873
CH_2 Rocking + HC-COO Stretching				842
CH2 Rocking + H Imidazole Bending out of plane		826		
C-N$(CH_3)_3$ Stretching	875/820	873		811
H_2C-C Stretching Imidazole			733	
(C=)C-H Bending out of plane		764	710	757
(C=)C-H Bending out of plane + C-N$(CH_3)_3$ Stretching		733	811	710
COO Wagging			679	
Imidazole Torsion		987		687
Imidazole Bending out of plane		625		625

Accurate ion masses determined of the following molecular ions:

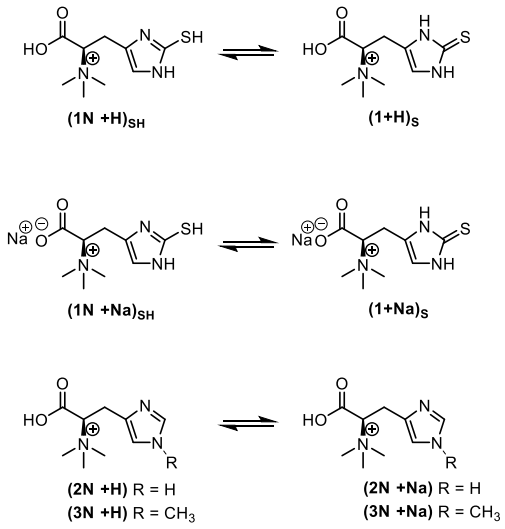


Table S7: Accurate masses of the probed molecular ions with composition and experimental error.

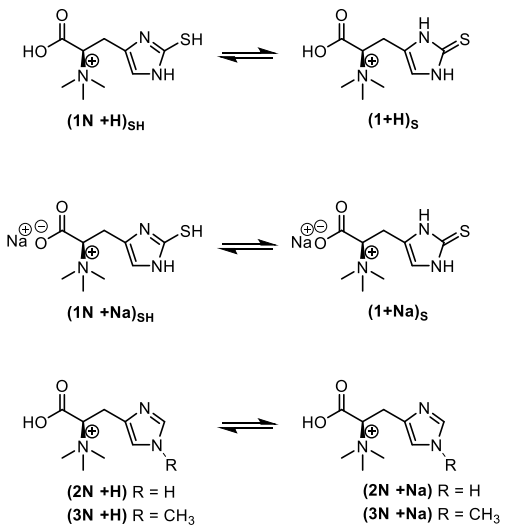
Molecular ion	Theoretical mass (u)	Experimental mass (u)	Difference (mmu)
$[1+H]^+$ $[C_9H_{16}O_2N_3S]^+$	230.09577	230.0957	0.00261
$[1+Na]^+$ $[C_9H_{15}O_2N_3NaS]+$	252.0777	252.0776	-0.02940
$[2+H]^+$ $[C_9H_{16}O_2N_3]^+$	198.12370	198.12391	0.20503
$[2+Na]^+$ $[C_9H_{15}O_2N_3Na]^+$	220.10565	220.10583	0.17918
$[3+H]^+$ $[C_{10}H_{18}O_2N_3]^+$	212.13935	212.13774	-1.61552
$[3+Na]^+$ $[C_{10}H_{17}O_2N_3Na]+$	234.12130	234.11967	-1.62716

Table S8: Product ions used for IRMPD experiments of the following molecular ions.

Precursor ion species	IRMPD Product ions	Neutral Loss
$(1N\varepsilon+H)_{SH}/(1+H)_S$ *m/z* 230	60 ($HNMe_3^+$) 99 100 127 186	170 Da 131 Da (NMe_3, CO_2, C_2H_4) 130 Da (CH_2NMe_2, CO_2, C_2H_4) 103 Da (NMe_3, CO_2) 44 Da (CO_2)
$(2N\varepsilon+H)$ *m/z* 198	60 ($HNMe_3^+$) 95 154	138 Da 103 Da (NMe_3, CO_2) 44 Da (CO_2)
$(3N\varepsilon+H)$ *m/z* 212	153 168	59 Da (NMe_3) 44 Da (CO_2)
$(1N\varepsilon+Na)_{SH}/(1+Na)_S$ *m/z* 252	99 149 165	153 Da (NMe_3, CO_2, C_2H_4, Na^+) 103 Da (NMe_3 & CO_2) 87 Da
$(2N\varepsilon+Na)$ *m/z* 220	117 133 161 176	103 Da (NMe_3 & CO_2) 87 Da 59 Da (NMe_3) 44 Da (CO_2)
$(3N\varepsilon+Na)$ *m/z* 234	131 147 160 175 190	103 Da (NMe_3, CO_2) 87 Da 74 Da (NMe_3, $\bullet CH_3$) 59 Da (NMe_3) 44 Da (CO_2)

S3. COMPUTATIONAL SUMMARY

Coordinates of the three isomers **a, b, c** identified by theory of each of the analyte complex ions included in the study:



Protonated ET $(1+H)_S$ thione structure **a** at 26.2 kJmol^{-1} **$(1N\varepsilon+H)_{SH}$** thiol structures **b** at 0 kJmol^{-1}, **c** at 3.9 kJmol^{-1} and **c2** at 4.8 kJmol^{-1}

Sodiated ET thiols **$(1N\varepsilon+Na)_{SH}$ a** at 42.8 kJmol^{-1}, **b** at 18.4 kJmol^{-1} and ET thione **$(1+Na)_S$** structure **c** at 0.0 kJmol^{-1}

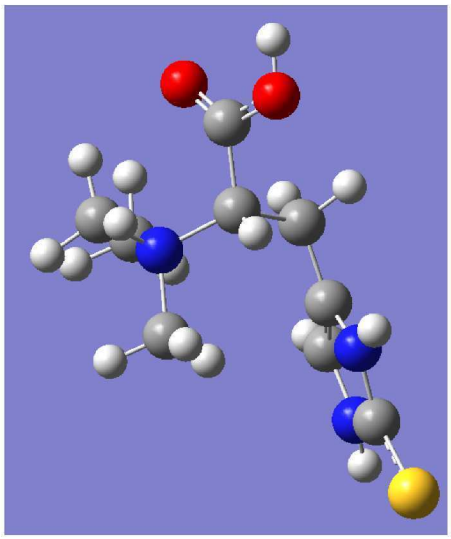
Protonated hercynine **(2Nε+H)** ion structure **a** at 11.3 kJmol^{-1} **b** at 5.2 kJmol^{-1} and structure **c** at 0.0 kJmol^{-1}.

Sodiated hercynine **(2Nε+Na)** ion structures **a** (16.2 kJmol^{-1}), **b** (13.2 kJmol^{-1}), **c** (0.0 kJmol^{-1})

Protonated *N*ε-Methyl-hercynine **(3Nε+H)** ion structures **a** at 14.0 kJmol^{-1}, **b** at 7.4 kJmol^{-1} and **c** at 0.0 kJmol^{-1}

Sodiated *N*ε-Methyl-Hercynine **(3Nε+Na)** ion structures **a** at 15.3 kJmol^{-1}, **b** at 15.1 kJmol^{-1} and **c** at 0.0 kJmol^{-1}

S4. ERGOTHIONINE $(1+H)_S$ (THIONE; ISOMER A)



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	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.59676147	a.u.
Gibbs Energy	: -1065.37833900	a.u.
Number of imaginary frequencies	: 0	

S4.1. Cartesian Co-ordinates (XYZ format)

31

C	1.64597702	0.17393699	1.74658895
C	0.91077697	-0.51892000	0.84719300
C	3.00559711	-0.22725600	-0.04451100
N	2.90312004	0.35273001	1.19985497
H	1.37974000	0.54470402	2.71953893
N	1.74142206	-0.74948400	-0.24508999
S	4.30123091	-0.28410101	-1.06254005
C	-0.51059300	-0.93872702	0.88054699
H	-0.93994898	-0.70332903	1.85217798
H	-0.57973802	-2.02510595	0.77525997
C	-1.42139804	-0.38619301	-0.24681801
H	-1.00822496	-0.65063602	-1.21656406
N	-1.58928096	1.13876998	-0.29728901
C	-2.76821399	-1.09026301	-0.08438400
O	-3.67482305	-0.69707298	0.59817600
O	-2.75242996	-2.24145293	-0.75780499
C	-0.33337000	1.77197194	-0.84553802
H	0.48936000	1.58425796	-0.16999801
H	-0.12396600	1.35139704	-1.82396305
H	-0.51355398	2.83885503	-0.93136102

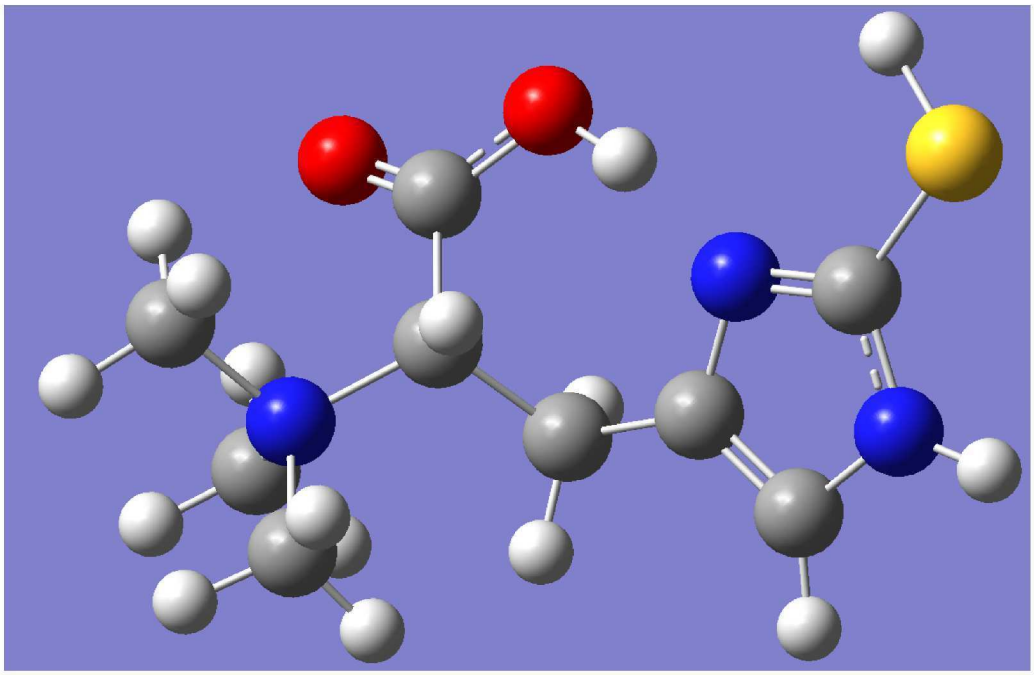
C	-1.88355899	1.73535597	1.05322897
H	-2.75496411	1.24453795	1.46947300
H	-1.01546597	1.60415697	1.68861496
H	-2.07335997	2.79485297	0.91082901
C	-2.70927000	1.49076998	-1.24640596
H	-2.69756508	2.56596994	-1.39247298
H	-2.53135395	0.99039400	-2.19441700
H	-3.65458393	1.18245101	-0.81909698
H	-3.57524896	-2.72708702	-0.58003300
H	3.69436097	0.78897601	1.64154506
H	1.56411600	-1.35488701	-1.02810705

S4.2. Frequencies

Mode	IR frequency	IR intensity
1	35.63550000	3.64890000
2	41.38270000	5.80940000
3	56.46510000	0.87710000
4	78.45510000	2.06190000
5	99.24890000	0.86990000
6	165.17820000	4.67640000
7	174.68950000	3.35270000
8	215.09810000	1.60030000
9	226.44840000	0.89740000
10	259.58850000	1.59100000
11	277.73630000	0.77580000
12	289.02680000	0.53570000
13	307.05450000	0.90580000
14	318.77400000	1.20840000
15	343.44650000	4.32100000
16	355.63080000	2.20420000
17	397.37540000	0.22240000
18	419.23660000	0.99700000
19	436.34240000	1.52680000
20	476.77920000	2.75890000
21	494.37370000	41.49800000
22	521.96580000	9.79390000
23	562.80300000	31.17980000
24	580.04120000	79.79700000
25	617.98020000	56.40650000
26	647.22450000	54.32630000
27	660.56430000	46.43980000
28	675.78350000	10.85870000
29	716.49500000	15.16620000
30	740.65470000	2.96700000
31	793.72100000	44.66290000
32	799.52050000	19.33660000
33	851.24020000	22.75430000
34	911.50300000	21.95060000
35	938.08900000	34.05900000
36	966.00010000	18.87790000
37	974.40920000	10.69370000
38	1001.95050000	14.37950000
39	1010.53960000	16.38700000
40	1037.93030000	0.86200000
41	1077.52620000	0.22450000
42	1102.37800000	67.06050000
43	1136.72650000	36.40500000
44	1147.52690000	10.29930000
45	1167.63470000	162.46390000
46	1178.05240000	138.89360000
47	1206.62150000	13.04100000

48	1220.00970000	1.70740000
49	1253.25600000	13.80150000
50	1272.66390000	0.80040000
51	1287.56580000	13.57030000
52	1295.29250000	7.52340000
53	1306.91260000	24.05600000
54	1361.32290000	71.58120000
55	1366.79840000	5.72890000
56	1390.94780000	14.13610000
57	1420.48920000	10.06940000
58	1424.35320000	46.06270000
59	1446.73880000	13.60320000
60	1449.00680000	1.15020000
61	1476.48380000	18.41860000
62	1481.57630000	6.56880000
63	1492.30910000	83.78190000
64	1496.78410000	14.65550000
65	1500.91890000	2.91500000
66	1509.52810000	333.39340000
67	1513.97270000	184.88810000
68	1519.98690000	21.22840000
69	1536.84930000	45.00540000
70	1672.18270000	6.56890000
71	1824.66860000	261.53290000
72	3031.08290000	7.48990000
73	3080.59080000	0.51420000
74	3085.75550000	2.80080000
75	3090.03690000	4.97770000
76	3103.43600000	0.46290000
77	3117.64910000	1.23090000
78	3163.06730000	0.32060000
79	3170.15960000	1.56040000
80	3173.67070000	1.80240000
81	3195.37890000	2.19240000
82	3199.58550000	2.89380000
83	3208.43440000	7.46670000
84	3269.39430000	5.93760000
85	3647.48790000	77.39000000
86	3652.13090000	119.21880000
87	3707.28610000	174.12610000

S5. ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER B)



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Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.60307476	a.u.
Gibbs Energy	: -1065.38832400	a.u.
Number of imaginary frequencies	: 0	

S5.1. Cartesian Co-ordinates (XYZ format)

31

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C	-0.95986801	0.91549999	-0.60880297
C	-2.90134192	0.17243899	0.01740900
N	-3.03598690	1.49411297	-0.25687999
H	-1.65949595	3.01209307	-0.92322701
N	-1.65188706	-0.20287099	-0.18133700
S	-4.24327993	-0.79868501	0.58722699
C	0.49308601	0.81690401	-0.95212901
H	0.90314299	1.82207298	-0.98629302
H	0.62045503	0.39884400	-1.95261097
C	1.25023603	-0.07178300	0.06836500
H	0.72108698	-0.04723400	1.01923800
N	2.65112996	0.45201001	0.41202199
C	1.27981806	-1.53948903	-0.42971501
O	2.30059695	-2.08485293	-0.77014601

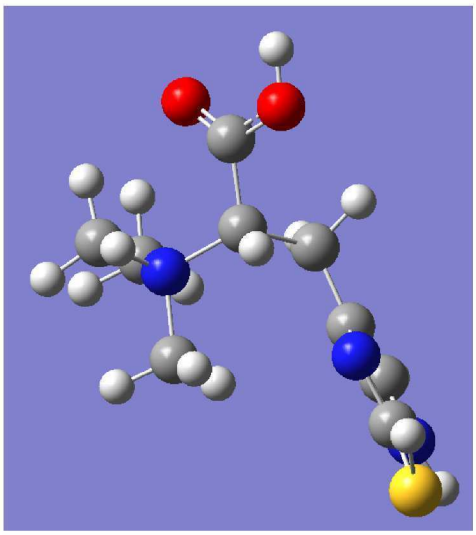
O	0.10664400	-2.11920500	-0.46581301
C	2.52240705	1.78810894	1.08741200
H	2.10110211	2.51537991	0.40489200
H	1.88576198	1.68223703	1.96070397
H	3.51373792	2.11085796	1.38910604
C	3.52824497	0.59793800	-0.80393600
H	3.62948298	-0.37405300	-1.26924396
H	3.07309508	1.30871403	-1.48520195
H	4.49245787	0.97386402	-0.47510299
C	3.32110810	-0.47441500	1.40091097
H	4.24960518	-0.00852900	1.71561694
H	2.66148305	-0.59788299	2.25535798
H	3.50928497	-1.42429805	0.92066300
H	-3.64487004	-1.96966505	0.30878100
H	-0.66777098	-1.49310303	-0.26008201
H	-3.89407802	2.01875901	-0.21280099

S5.2. Frequencies

Mode	IR frequency	IR intensity
1	36.45090000	0.98470000
2	49.57700000	1.56110000
3	82.22390000	1.75520000
4	91.70090000	11.98000000
5	107.50510000	6.17350000
6	121.23020000	4.32200000
7	171.45950000	9.37040000
8	193.53710000	1.98580000
9	230.08350000	4.24660000
10	253.35680000	6.54140000
11	257.84500000	0.71680000
12	266.83810000	9.04240000
13	280.51600000	2.60750000
14	302.39170000	11.15130000
15	331.58270000	5.39780000
16	336.81650000	10.19590000
17	363.79420000	6.65420000
18	384.26260000	3.43800000
19	430.43070000	2.94110000
20	439.82580000	0.57620000
21	473.83020000	0.35140000
22	494.59510000	1.10630000
23	553.76190000	3.23000000
24	581.88820000	79.00200000
25	644.38370000	3.34040000
26	675.84900000	10.33450000
27	700.69990000	1.12440000
28	735.61690000	1.22680000
29	759.42980000	9.80020000
30	776.47100000	19.63820000
31	811.76400000	24.96590000
32	848.60720000	6.70280000
33	906.85280000	50.68910000
34	927.72590000	21.87570000
35	943.98970000	18.90580000
36	971.50000000	16.63330000
37	998.60460000	16.83410000
38	1013.31410000	31.48440000
39	1024.43760000	6.81980000
40	1035.44850000	11.43550000
41	1048.78320000	26.14520000
42	1075.32430000	0.36610000

43	1118.08640000	40.81190000
44	1138.68500000	3.49850000
45	1149.83910000	3.92640000
46	1204.63940000	3.63830000
47	1234.53760000	6.19290000
48	1241.92490000	30.89600000
49	1254.38410000	57.14760000
50	1277.67060000	57.10010000
51	1295.01530000	8.88210000
52	1296.56100000	1.97000000
53	1327.14270000	16.48320000
54	1349.11400000	20.86100000
55	1367.97880000	18.14230000
56	1414.46720000	10.21760000
57	1438.90840000	11.74720000
58	1447.53770000	26.18220000
59	1451.59440000	57.18520000
60	1475.51040000	1.24140000
61	1484.10800000	28.09550000
62	1491.96560000	3.76280000
63	1496.37510000	3.25690000
64	1507.55930000	9.24720000
65	1508.78750000	8.20400000
66	1514.45560000	33.78880000
67	1524.28160000	43.33340000
68	1526.40450000	301.26870000
69	1539.48150000	35.95100000
70	1619.71900000	51.75170000
71	1814.39410000	397.81900000
72	2690.10250000	4.75880000
73	2779.34120000	2014.41000000
74	3044.38300000	7.86840000
75	3079.58980000	2.95680000
76	3083.41130000	1.33900000
77	3086.53030000	6.37890000
78	3090.58730000	3.87380000
79	3119.82130000	7.12530000
80	3160.61560000	0.77350000
81	3166.88150000	1.63930000
82	3169.98500000	4.43470000
83	3188.60700000	3.34000000
84	3199.05880000	4.67720000
85	3210.65520000	9.50010000
86	3276.37580000	4.21230000
87	3637.40310000	119.24870000

S6. ERGOTHIONINE ($1N\varepsilon+H)_{SH}$ (THIOL; ISOMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.59993352	a.u.
Gibbs Energy	: -1065.38682100	a.u.
Number of imaginary frequencies	: 0	

S6.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.76267898	0.26136500	1.97699904
C	-0.92081100	0.54472798	0.94027197
C	-2.84363604	0.18195200	0.04578800
N	-2.99432206	0.03704400	1.39137602
H	-1.61999094	0.22395401	3.04151893
N	-1.59950197	0.48281401	-0.25961000
S	-4.18526983	-0.06833700	-1.05942297
C	0.52136600	0.93082201	0.96469897
H	0.98189998	0.70425701	1.92441297
H	0.59406400	2.01399302	0.84437197
C	1.34262300	0.35211599	-0.20296900
H	0.74384999	0.45325699	-1.10519195
N	1.67283106	-1.14502203	-0.10717700
C	2.60841203	1.19131899	-0.35422999
O	3.69023800	0.92842501	0.10077600
O	2.32181096	2.30306911	-1.03485501
C	0.40849701	-1.95651996	-0.23030201
H	-0.21860600	-1.77340806	0.63246900
H	-0.11850000	-1.65867496	-1.12993097
H	0.69397902	-3.00288796	-0.27699000
C	2.35059309	-1.51964498	1.18332899

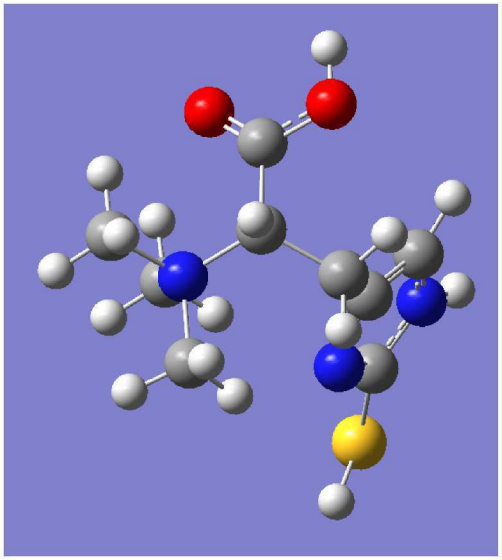
H	3.24274707	-0.91767502	1.29990995
H	1.65976095	-1.35639501	2.00240302
H	2.60246491	-2.57448792	1.12833703
C	2.56195402	-1.52834105	-1.26285195
H	2.67348909	-2.60780501	-1.25858796
H	2.08349800	-1.21160996	-2.18530512
H	3.52776504	-1.05380201	-1.14658201
H	3.11246991	2.86621308	-1.06226397
H	-3.58808494	0.57988900	-2.07378888
H	-3.85733199	-0.14640801	1.87566495

S6.2. Frequencies

Mode	IR frequency	IR intensity
1	10.74730000	1.00690000
2	45.13750000	3.06660000
3	59.46750000	1.88070000
4	70.92620000	2.61570000
5	96.56520000	0.94480000
6	125.16860000	15.76250000
7	182.81750000	0.70820000
8	184.94400000	22.53020000
9	221.87090000	1.98350000
10	228.98510000	3.99330000
11	262.71510000	0.83010000
12	271.95580000	0.96490000
13	295.99080000	1.17490000
14	298.69630000	1.57500000
15	315.52770000	2.38410000
16	348.36340000	3.36850000
17	361.55730000	8.79040000
18	376.22830000	8.67990000
19	427.88150000	1.52900000
20	434.64230000	1.92690000
21	472.93970000	0.15410000
22	487.88730000	1.28480000
23	559.52220000	29.45050000
24	563.46280000	52.96320000
25	614.82120000	73.43360000
26	651.13980000	24.96570000
27	661.58790000	47.52670000
28	701.18510000	6.63300000
29	724.93870000	8.98690000
30	747.20060000	7.73590000
31	771.41770000	23.12580000
32	798.88750000	17.54410000
33	857.68040000	24.33950000
34	910.53350000	14.68700000
35	918.60060000	23.76940000
36	946.38000000	25.79790000
37	969.71370000	16.63790000
38	995.81120000	5.45190000
39	1006.29780000	35.28450000
40	1023.12970000	4.17950000
41	1055.97000000	0.81520000
42	1081.33490000	0.05310000
43	1109.17080000	27.58940000
44	1137.67770000	32.96030000
45	1149.29990000	22.59200000
46	1169.34810000	155.48420000
47	1197.18630000	18.99560000
48	1232.28430000	17.02250000

49	1253.53250000	19.53910000
50	1274.57680000	1.98510000
51	1292.61850000	4.92790000
52	1294.71170000	1.81150000
53	1303.10560000	2.55690000
54	1337.43120000	41.77610000
55	1362.39610000	45.23660000
56	1386.03790000	35.10090000
57	1431.00780000	9.94510000
58	1438.21630000	31.18680000
59	1446.84690000	21.80340000
60	1454.71150000	1.56670000
61	1472.54120000	7.07500000
62	1481.03470000	7.09460000
63	1492.10990000	39.74860000
64	1498.17130000	6.34430000
65	1502.26260000	2.03190000
66	1513.42490000	30.72720000
67	1514.27220000	96.15850000
68	1519.22760000	28.95180000
69	1537.35930000	56.14280000
70	1606.95570000	10.71290000
71	1818.14480000	273.76740000
72	2692.78780000	4.71180000
73	3045.19120000	4.75240000
74	3081.00660000	1.16090000
75	3084.75190000	2.76840000
76	3089.70430000	8.23230000
77	3099.70970000	8.80520000
78	3112.90600000	2.79070000
79	3163.90370000	1.07140000
80	3170.52710000	1.82220000
81	3176.31300000	1.82250000
82	3193.26640000	1.52640000
83	3196.76900000	0.15300000
84	3200.99720000	5.26190000
85	3269.16680000	2.57450000
86	3638.28650000	108.86900000
87	3716.61840000	156.99980000

S7. ERGOTHIONINE (1Nε+H)$_{SH}$ (THIOL; ISOMER C2)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.60107865	a.u.
Gibbs Energy	: -1065.38649200	a.u.
Number of imaginary frequencies	: 0	

S7.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.68987799	-1.15685999	3.31762409
C	-1.10618901	-0.23975401	2.49124408
C	-1.81854796	0.87025303	4.19787884
N	-2.13935995	-0.43686801	4.40466309
H	-1.80317104	-2.22309208	3.24935508
N	-1.19840503	1.02478194	3.04730606
S	-2.26396704	2.11643696	5.35310078
C	-0.41117600	-0.45064500	1.19040298
H	-0.06333000	-1.47866595	1.12486506
H	0.47984299	0.17150800	1.15401495
C	-1.22921896	-0.23562101	-0.10182200
H	-0.54946798	-0.44592401	-0.92905599
N	-1.70401704	1.19960701	-0.37970701
C	-2.36535001	-1.25272000	-0.24238700
O	-3.50006199	-1.02028298	-0.55943799
O	-1.89430702	-2.48238111	-0.00732200
C	-0.57490599	2.15543008	-0.09962900
H	-0.40740001	2.19621801	0.97143501
H	0.31525299	1.82217395	-0.62574100
H	-0.87359101	3.13183093	-0.46771100

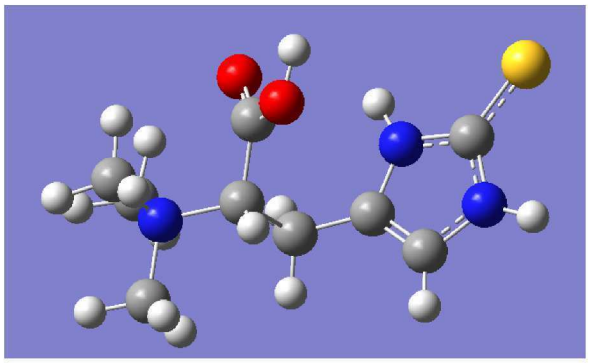
C	-2.89226103	1.65055001	0.44378000
H	-3.73459911	1.00994301	0.22681800
H	-2.61531997	1.61734998	1.48975098
H	-3.10547090	2.67364192	0.14825800
C	-2.06139898	1.31340206	-1.83952606
H	-2.36258006	2.33798194	-2.03283405
H	-1.18611705	1.06909299	-2.43479300
H	-2.87868905	0.63730800	-2.05662203
H	-2.61440802	-3.11608100	-0.15619899
H	-1.32162905	2.97721100	4.93239880
H	-2.56488204	-0.81683898	5.23392677

S7.2. Frequencies

Mode	IR frequency	IR intensity
1	26.49060000	2.48500000
2	39.42400000	3.22290000
3	58.72050000	1.92570000
4	68.43220000	1.91640000
5	111.03050000	17.99870000
6	118.87760000	1.87900000
7	168.11290000	5.34610000
8	209.08910000	10.85640000
9	225.51550000	1.52820000
10	242.63700000	8.97290000
11	268.35830000	0.57350000
12	280.58880000	0.41410000
13	310.07310000	6.40890000
14	323.26680000	3.53580000
15	340.95750000	5.76870000
16	355.67320000	0.35920000
17	369.60150000	7.78000000
18	412.84310000	1.00090000
19	434.01270000	3.42490000
20	441.44840000	2.16900000
21	471.58130000	0.46360000
22	523.57350000	12.47860000
23	548.92480000	11.22880000
24	573.24900000	66.09830000
25	601.63760000	37.73170000
26	650.52870000	62.47950000
27	659.55050000	20.63240000
28	685.35890000	9.93890000
29	707.82000000	22.08180000
30	730.37290000	10.87360000
31	779.83170000	22.10880000
32	805.94140000	22.23990000
33	864.83300000	3.09710000
34	886.74850000	37.60750000
35	918.53350000	20.54030000
36	951.64030000	19.51580000
37	960.43490000	11.24210000
38	987.10860000	13.56240000
39	1009.11730000	14.89070000
40	1013.59310000	4.65760000
41	1047.05870000	17.93270000
42	1085.84400000	0.46170000
43	1112.20520000	32.67760000
44	1144.97510000	33.84380000
45	1149.80960000	40.70620000
46	1172.86900000	158.17920000
47	1205.53840000	3.18460000

48	1240.92930000	9.79380000
49	1253.07010000	5.69840000
50	1261.65770000	2.05180000
51	1292.41950000	1.15470000
52	1298.68400000	1.14110000
53	1312.92720000	9.64090000
54	1343.05120000	12.79370000
55	1359.67220000	27.81090000
56	1403.03030000	3.96450000
57	1414.06900000	17.12980000
58	1433.22030000	44.36970000
59	1448.45970000	4.45980000
60	1452.04640000	4.18830000
61	1481.70730000	20.67900000
62	1482.74330000	3.63830000
63	1493.56650000	18.10580000
64	1501.67370000	9.98790000
65	1506.40680000	1.01960000
66	1513.51470000	86.53230000
67	1518.30590000	36.56650000
68	1526.89500000	22.41920000
69	1544.57500000	31.41380000
70	1607.00030000	8.97960000
71	1822.16340000	237.69360000
72	2691.73170000	3.90090000
73	3060.43240000	1.82830000
74	3069.76660000	4.33850000
75	3080.90730000	2.53700000
76	3090.00160000	19.83250000
77	3092.07470000	18.22610000
78	3127.20700000	1.11880000
79	3159.68420000	0.33870000
80	3165.15890000	5.35300000
81	3170.30220000	1.10650000
82	3176.16020000	22.50300000
83	3195.52510000	1.88460000
84	3219.88740000	18.33360000
85	3273.72650000	2.38830000
86	3637.96380000	108.86170000
87	3721.14980000	149.08560000

S8. ERGOTHIONINE (1+H)$_S$ (THIONE; ISOMER A2)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.59572968	a.u.
Gibbs Energy	: -1065.37793700	a.u.
Number of imaginary frequencies	: 0	

S8.1. Cartesian Co-ordinates (XYZ format)

31

C	1.60981297	1.92193496	-0.50631601
C	0.88072997	1.10332501	0.28523201
C	2.98056412	0.20349400	0.10694300
N	2.87359309	1.37568605	-0.60495198
H	3.65727592	1.75980401	-1.10412800
H	1.33359396	2.83442211	-1.00189602
N	1.72396195	0.05677800	0.65066999
S	4.28287506	-0.80075502	0.26812100
C	-0.56222600	1.12851703	0.64778697
H	-0.92458302	2.15110993	0.57173997
H	-0.68747801	0.79965103	1.67920804
C	-1.37193596	0.20996000	-0.29245299
H	-1.30929303	0.58554697	-1.30941701
N	-2.87845993	0.16275001	0.01966000
C	-0.77944702	-1.20125699	-0.25201401
O	-0.21764000	-1.51205695	-1.41561198
O	-0.80143201	-1.90220201	0.72583503
C	-3.48633289	1.49372697	-0.32288799
H	-3.04974008	2.26369905	0.30219001
H	-3.30302191	1.70747900	-1.37167203
H	-4.55446005	1.43754303	-0.13669500
C	-3.17790604	-0.15329100	1.46298397
H	-2.66175890	-1.06562102	1.73690903
H	-2.84893107	0.67217702	2.08354402
H	-4.25309086	-0.27297699	1.55631304
C	-3.52391911	-0.88392597	-0.85027403
H	-4.60054779	-0.81055701	-0.73288703

H	-3.24737000	-0.70169997	-1.88457894
H	-3.18772888	-1.86546004	-0.53377002
H	1.52675796	-0.68079197	1.30563200
H	0.24880500	-2.36178088	-1.33411300

S8.2. Frequencies

Mode	IR frequency	IR intensity
1	27.98450000	0.12560000
2	43.35890000	2.25890000
3	56.76680000	0.24580000
4	65.29840000	1.99020000
5	94.41590000	2.70930000
6	159.98360000	1.56700000
7	182.91200000	5.06510000
8	187.58940000	3.14730000
9	223.44480000	2.25820000
10	242.55670000	3.93360000
11	261.76670000	0.26830000
12	283.27370000	1.48680000
13	292.46350000	1.11320000
14	317.43340000	0.36720000
15	333.15220000	4.30470000
16	345.50510000	3.40000000
17	389.96300000	1.30240000
18	431.52790000	0.92640000
19	432.38870000	0.78920000
20	460.82970000	0.80860000
21	513.37480000	40.22630000
22	520.92580000	9.52520000
23	547.15050000	12.27980000
24	581.79510000	124.05670000
25	637.05240000	48.71970000
26	650.61060000	40.94440000
27	663.87550000	22.00960000
28	683.03930000	12.44690000
29	723.29480000	32.20760000
30	743.65390000	37.82350000
31	788.81470000	22.47570000
32	816.46050000	34.37840000
33	828.80370000	25.18840000
34	907.36170000	26.75680000
35	953.31750000	22.14790000
36	964.97230000	13.43870000
37	977.52200000	13.81690000
38	999.71810000	5.63740000
39	1022.34050000	1.76120000
40	1046.99380000	0.11470000
41	1080.43470000	0.04250000
42	1105.08200000	62.46820000
43	1137.52650000	21.94780000
44	1151.67400000	0.68390000
45	1169.08060000	111.70120000
46	1179.00880000	125.18090000
47	1202.32870000	42.61350000
48	1229.15960000	3.50340000
49	1247.77240000	4.85290000
50	1266.27250000	3.95870000
51	1288.99090000	7.55330000
52	1298.74640000	33.69630000
53	1317.44320000	5.76130000
54	1349.20930000	10.39470000

55	1369.00250000	13.13650000
56	1381.59870000	9.90410000
57	1425.27450000	3.52860000
58	1433.98950000	16.58730000
59	1451.52300000	14.13370000
60	1453.67320000	4.59320000
61	1479.44490000	11.86560000
62	1483.98840000	11.27780000
63	1491.34020000	8.24110000
64	1496.95570000	1.29870000
65	1499.49100000	2.63270000
66	1511.50960000	23.37220000
67	1512.75540000	579.64840000
68	1519.33210000	21.64330000
69	1533.23700000	45.92130000
70	1669.57950000	11.84840000
71	1814.14230000	209.03250000
72	3061.81670000	13.20800000
73	3077.45520000	0.30230000
74	3081.18470000	0.48460000
75	3088.09720000	6.21560000
76	3113.60530000	1.17210000
77	3127.00130000	1.43010000
78	3164.42240000	0.02700000
79	3168.94340000	1.12570000
80	3173.44210000	1.33070000
81	3176.89190000	0.23970000
82	3184.32120000	1.11340000
83	3194.33660000	4.81590000
84	3272.03950000	4.62480000
85	3643.91720000	78.76720000
86	3655.94720000	121.54070000
87	3694.69640000	126.30700000

S9. ERGOTHIONINE $(1+H)_S$ (THIONE; ISOMER A; ω-B97X-D)

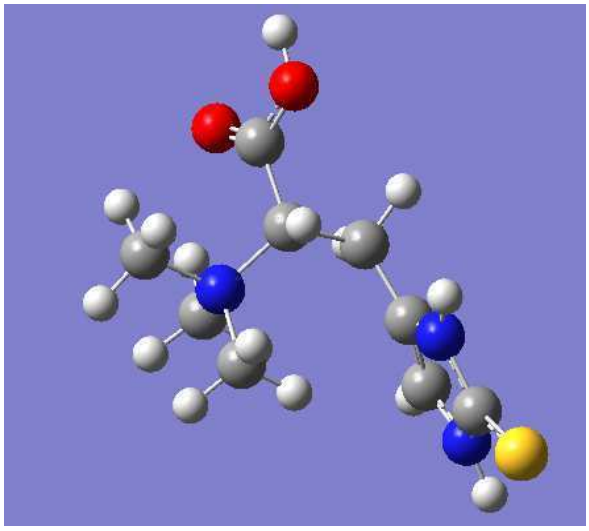


FIG. S1. Molecule

Route	: # opt freq wb97xd/cc-pvtz geom=connectivity int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.31031255	a.u.
Gibbs Energy	: -1065.08814700	a.u.
Number of imaginary frequencies	: 0	

S9.1. Cartesian Co-ordinates (XYZ format)

31

C	1.62742603	0.24663900	1.76003897
C	0.90767097	-0.47308999	0.87818497
C	2.99652100	-0.19666900	0.00158700
N	2.88529301	0.41444901	1.22009397
H	1.35155404	0.64327800	2.72043300
N	1.74750602	-0.73294801	-0.19450000
S	4.29752588	-0.26851100	-1.00811803
C	-0.51199299	-0.90160298	0.91120303
H	-0.95148897	-0.63785797	1.87174201
H	-0.56783998	-1.99154198	0.84356499
C	-1.41240704	-0.39361101	-0.23803701
H	-0.99347299	-0.69279701	-1.19663799
N	-1.59077299	1.11837399	-0.34312901
C	-2.75388503	-1.10565603	-0.05624200
O	-3.64433599	-0.71736699	0.64398301
O	-2.75062299	-2.24656796	-0.73051602
C	-0.35433099	1.73631406	-0.93125498
H	0.48550901	1.57410598	-0.26797101
H	-0.16079900	1.28963006	-1.90241396
H	-0.53683698	2.80085802	-1.04512000

C	-1.86727798	1.76164496	0.98097599
H	-2.72255898	1.27546895	1.43737900
H	-0.98433900	1.67228305	1.60527694
H	-2.07917404	2.81195307	0.80174398
C	-2.72159696	1.42486298	-1.28288603
H	-2.71573091	2.49234796	-1.48092997
H	-2.56240106	0.88116401	-2.21112895
H	-3.66144490	1.13891304	-0.82580203
H	-3.56533599	-2.73147893	-0.53866500
H	3.66868401	0.87190199	1.65129995
H	1.57665002	-1.34968305	-0.96870100

S9.2. Frequencies

Mode	IR frequency	IR intensity
1	41.21370000	4.44340000
2	43.50610000	6.19260000
3	56.54490000	0.99450000
4	80.59190000	1.79390000
5	101.30400000	0.90780000
6	169.64220000	3.52410000
7	176.50660000	4.09080000
8	219.24760000	1.55630000
9	235.06540000	1.08100000
10	267.42290000	1.38580000
11	291.74070000	1.15990000
12	302.98470000	0.29070000
13	318.92590000	1.34340000
14	331.95010000	0.90500000
15	354.13110000	5.33890000
16	366.92810000	1.29850000
17	404.27570000	0.36890000
18	431.83520000	0.93720000
19	451.06490000	1.31010000
20	490.30580000	2.82160000
21	515.06530000	44.07710000
22	528.05260000	8.32860000
23	577.15280000	23.07600000
24	599.74380000	90.28120000
25	627.64720000	55.99340000
26	657.55890000	63.69440000
27	673.15350000	47.37600000
28	693.68550000	6.94380000
29	726.97010000	15.89540000
30	757.84620000	4.42700000
31	812.35210000	12.88120000
32	816.61050000	52.86270000
33	880.49450000	17.77000000
34	930.37430000	20.14920000
35	971.78060000	31.20330000
36	990.17790000	13.09040000
37	994.92030000	13.87670000
38	1018.85990000	5.07490000
39	1037.89390000	24.94740000
40	1057.18410000	1.34460000
41	1086.57080000	0.21430000
42	1119.14530000	55.52820000
43	1148.46520000	15.94200000
44	1159.93420000	2.47330000
45	1188.77230000	121.06950000
46	1194.27980000	192.82080000
47	1224.77490000	16.87620000
48	1252.79880000	0.38670000
49	1267.72880000	17.96960000
50	1291.53140000	1.27580000
51	1299.99910000	16.69770000
52	1314.82960000	18.44580000
53	1322.35660000	20.98620000
54	1382.57280000	21.85880000
55	1386.07660000	47.52730000
56	1410.36080000	12.87060000
57	1443.72800000	41.50770000
58	1448.22840000	35.06970000
59	1457.15560000	7.16420000
60	1458.99200000	16.58370000

61	1480.09720000	14.68460000
62	1486.08920000	3.48610000
63	1501.56570000	18.53270000
64	1502.45280000	24.26210000
65	1509.69530000	10.30150000
66	1519.67890000	12.82380000
67	1531.08570000	10.41920000
68	1546.14750000	415.80220000
69	1547.96450000	272.13920000
70	1707.50350000	6.67570000
71	1865.54860000	268.49380000
72	3060.65210000	5.57700000
73	3092.55880000	0.46300000
74	3097.03860000	2.58610000
75	3100.23990000	4.47790000
76	3123.91950000	0.06720000
77	3137.85660000	0.81380000
78	3184.70260000	0.20770000
79	3190.04880000	1.25310000
80	3193.46080000	1.19310000
81	3212.36700000	2.58400000
82	3216.76620000	1.92050000
83	3224.26670000	6.14940000
84	3291.80200000	6.68490000
85	3687.88620000	78.31230000
86	3693.37390000	126.36700000
87	3787.17040000	181.86810000

S10. ERGOTHIONINE $(1N\varepsilon+H)_{SH}$ (THIOL; ISOMER B; ω-B97X-D)

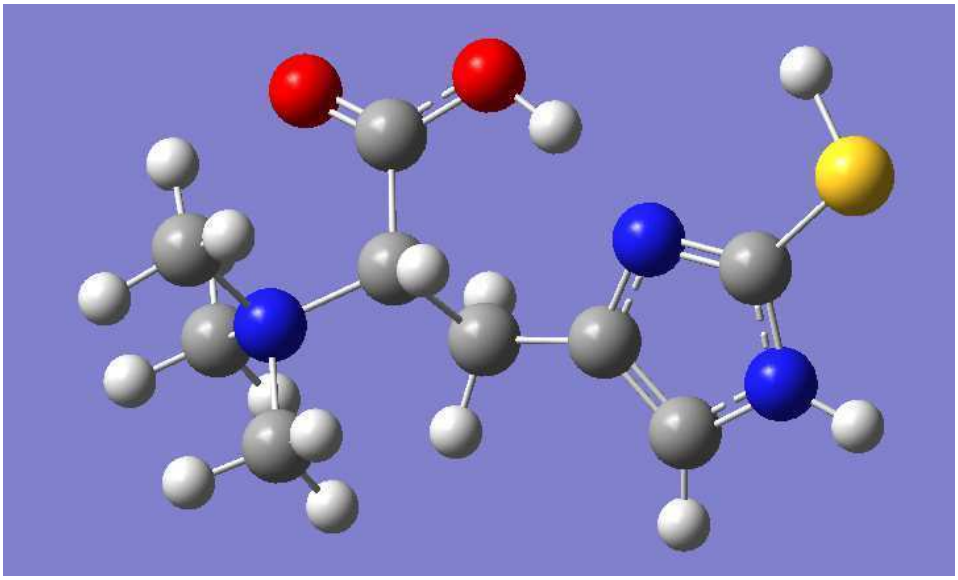


FIG. S2. Molecule

Route	: # opt freq wb97xd/cc-pvtz geom=connectivity int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.31616485	a.u.
Gibbs Energy	: -1065.09772900	a.u.
Number of imaginary frequencies	: 0	

S10.1. Cartesian Co-ordinates (XYZ format)

31

C	1.79771996	-1.95270002	-0.63884097
C	0.95645797	-0.88986999	-0.58260500
C	2.87355995	-0.16952200	0.08957400
N	3.01649809	-1.47566402	-0.21615601
H	1.65615594	-2.97361398	-0.94274998
N	1.63449895	0.21341500	-0.11617300
S	4.20186281	0.78581703	0.70896602
C	-0.49111000	-0.78609502	-0.94623101
H	-0.89634901	-1.79224598	-1.01180995
H	-0.60201001	-0.34615999	-1.93910503
C	-1.26393604	0.07610100	0.08156600
H	-0.73632199	0.04664400	1.03480101
N	-2.65226007	-0.46172199	0.40884799
C	-1.29921603	1.54929304	-0.39774400
O	-2.31341505	2.08915901	-0.75069499
O	-0.13614400	2.13897204	-0.40521300
C	-2.51433611	-1.79533899	1.07232594
H	-2.07593298	-2.51425004	0.39044699

H	-1.88970101	-1.68994296	1.95514596
H	-3.50453401	-2.13562799	1.36032104
C	-3.51565909	-0.60840702	-0.80747098
H	-3.62500691	0.36466199	-1.27121699
H	-3.05217195	-1.31232095	-1.49158597
H	-4.48000383	-0.99395102	-0.48835200
C	-3.33673596	0.44388300	1.39500999
H	-4.25891685	-0.03739600	1.70713699
H	-2.68264103	0.57696301	2.25313306
H	-3.54348302	1.39416695	0.92089897
H	3.65124393	1.95959902	0.36819899
H	0.63064897	1.52417195	-0.19134100
H	3.87476110	-1.99729800	-0.17327499

S10.2. Frequencies

Mode	IR frequency	IR intensity
1	42.42540000	0.84020000
2	51.93550000	1.80860000
3	85.09580000	0.33310000
4	100.14670000	11.20730000
5	108.77090000	8.79000000
6	120.86260000	6.36250000
7	174.46500000	9.45280000
8	193.74350000	1.88290000
9	233.14210000	4.72620000
10	252.12860000	8.62570000
11	267.57220000	1.38340000
12	272.18660000	7.25220000
13	288.60810000	2.72880000
14	307.91430000	10.28830000
15	340.57960000	8.92020000
16	343.69490000	6.47190000
17	371.28620000	5.75710000
18	391.51920000	3.56010000
19	439.46960000	2.75190000
20	452.44320000	0.45420000
21	483.02420000	0.10200000
22	504.68540000	1.30410000
23	567.71650000	2.95420000
24	608.35730000	84.01070000
25	653.72730000	3.09300000
26	690.12810000	9.04680000
27	711.95910000	1.48350000
28	746.76910000	0.80960000
29	773.72600000	8.19610000
30	798.34260000	19.90780000
31	834.84730000	20.34880000
32	861.80030000	6.90550000
33	938.11860000	47.69990000
34	941.17340000	28.02410000
35	976.86610000	12.82360000
36	998.20080000	39.03020000
37	1003.12810000	30.57350000
38	1018.99720000	7.90620000
39	1033.56090000	8.73370000
40	1040.73210000	13.60010000
41	1064.48290000	13.47070000
42	1083.83380000	0.64220000
43	1135.54870000	40.38240000
44	1147.26650000	3.31350000
45	1159.02800000	4.36900000
46	1218.65450000	5.31140000
47	1247.52930000	3.01090000
48	1259.04970000	22.82770000
49	1272.78670000	44.64620000
50	1297.80060000	36.95760000
51	1314.27990000	13.73380000
52	1316.47550000	1.14820000
53	1350.98150000	29.56300000
54	1372.50600000	13.43950000
55	1394.98570000	14.32220000
56	1434.86140000	7.67740000
57	1449.89270000	7.37230000
58	1455.35560000	20.98840000
59	1479.79610000	0.91570000
60	1491.35300000	77.66210000

61	1492.16860000	6.95740000
62	1498.03650000	5.14360000
63	1502.55660000	10.63850000
64	1510.92910000	1.66840000
65	1516.51830000	11.30160000
66	1522.30090000	143.49060000
67	1531.38550000	64.45760000
68	1546.72250000	117.50640000
69	1549.44170000	140.32160000
70	1650.15410000	49.72770000
71	1857.88850000	410.74570000
72	2742.56470000	5.87600000
73	2954.14260000	1868.66140000
74	3073.26600000	8.75080000
75	3093.33520000	2.56360000
76	3096.20990000	2.14060000
77	3099.53060000	8.20810000
78	3105.70890000	1.66900000
79	3146.81210000	5.71320000
80	3183.03860000	0.63180000
81	3188.34910000	1.25270000
82	3191.08720000	3.63050000
83	3208.42040000	2.77810000
84	3217.29630000	4.84070000
85	3231.38000000	9.00820000
86	3298.01630000	4.75710000
87	3682.10940000	128.59790000

S11. ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER C; ω-B97X-D)

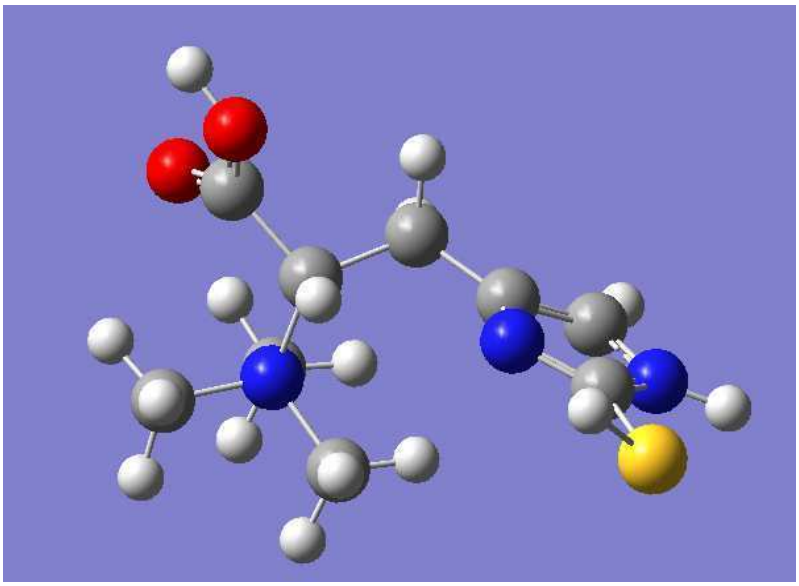


FIG. S3. Molecule

Route	: # opt freq wb97xd/cc-pvtz geom=connectivity int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.31452992	a.u.
Gibbs Energy	: -1065.09723100	a.u.
Number of imaginary frequencies	: 0	

S11.1. Cartesian Co-ordinates (XYZ format)

31

C	1.74659002	-0.04732800	1.93187201
C	0.92114902	-0.45226800	0.93023700
C	2.83110595	-0.15943301	0.02005100
N	2.97247601	0.13168600	1.33511305
H	1.59275496	0.10164500	2.98533106
N	1.60151196	-0.51046997	-0.26193699
S	4.17456722	-0.01260400	-1.09732997
C	-0.51609701	-0.84911102	0.99113798
H	-0.96950901	-0.57161897	1.94142997
H	-0.57338399	-1.93862998	0.93646699
C	-1.36067402	-0.35514900	-0.19415700
H	-0.80234998	-0.55259800	-1.10761404
N	-1.66418397	1.14146399	-0.22293900
C	-2.64264393	-1.18436396	-0.21042500
O	-3.67000198	-0.89252800	0.33521000
O	-2.43452311	-2.31459498	-0.87215298
C	-0.41288501	1.91152894	-0.52661300
H	0.28470001	1.80421805	0.29491800

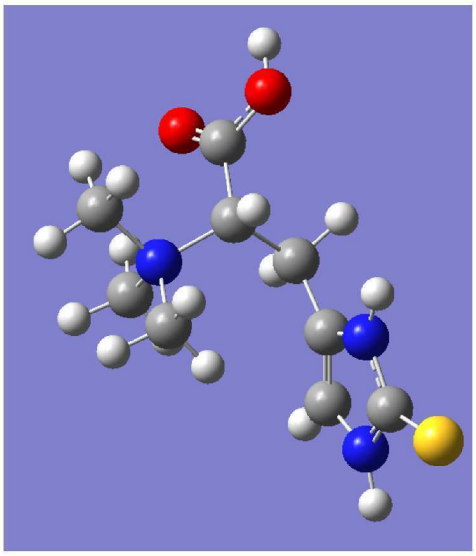
H	0.03523300	1.52195299	-1.43536496
H	-0.68893403	2.95468092	-0.65156299
C	-2.22762609	1.65107501	1.06720400
H	-3.10424209	1.06850302	1.32594204
H	-1.46773195	1.57505405	1.83793199
H	-2.49150991	2.69532609	0.92423600
C	-2.63539791	1.42393100	-1.33058202
H	-2.72568703	2.50065899	-1.43757999
H	-2.24620891	0.99608099	-2.25112700
H	-3.60008502	0.99598998	-1.08500600
H	-3.22520089	-2.86636090	-0.80298901
H	3.61759806	-0.81395400	-2.01577592
H	3.83002496	0.37553301	1.79876494

S11.2. Frequencies

Mode	IR frequency	IR intensity
1	22.48280000	1.26040000
2	48.29940000	3.38090000
3	61.11950000	1.99730000
4	69.97080000	2.33110000
5	97.23860000	0.93190000
6	113.51490000	20.32300000
7	179.83970000	0.62790000
8	188.44580000	19.13910000
9	227.31680000	3.32100000
10	237.95950000	3.28590000
11	270.52760000	0.90740000
12	279.46130000	1.25030000
13	305.78070000	0.71860000
14	315.92010000	0.78080000
15	328.08250000	4.40960000
16	360.21750000	6.90130000
17	373.01810000	7.70620000
18	397.30130000	5.83990000
19	441.55640000	1.21270000
20	447.94560000	1.74460000
21	479.95980000	0.13180000
22	499.29930000	1.64030000
23	574.86040000	14.81750000
24	588.45480000	71.10780000
25	625.43830000	74.16720000
26	663.21330000	28.71860000
27	675.40750000	48.85650000
28	713.19540000	8.15510000
29	736.73750000	8.99490000
30	766.38780000	5.29040000
31	797.35800000	26.34090000
32	813.05380000	16.68140000
33	888.03100000	20.05170000
34	924.47100000	10.68770000
35	933.23570000	28.33380000
36	980.53620000	25.12570000
37	997.03800000	18.10200000
38	1003.74430000	4.42970000
39	1027.85090000	10.76530000
40	1036.63730000	28.92860000
41	1073.17080000	1.15570000
42	1090.51620000	0.07400000
43	1127.61570000	31.14550000
44	1149.57490000	12.29060000
45	1158.21530000	11.62840000
46	1191.64790000	140.72450000
47	1213.58920000	47.67390000
48	1247.49680000	13.59140000
49	1267.05470000	21.33850000
50	1292.67660000	0.24740000
51	1306.33800000	0.94800000
52	1314.30020000	4.09710000
53	1321.59160000	1.11940000
54	1372.38830000	46.16020000
55	1386.33650000	33.97890000
56	1404.57040000	38.64590000
57	1452.34300000	19.61740000
58	1459.40200000	21.79490000
59	1463.01340000	8.22500000
60	1476.88680000	43.10560000

61	1479.08150000	5.76250000
62	1486.74680000	7.08440000
63	1499.10700000	19.83820000
64	1503.26760000	14.79670000
65	1513.02560000	9.79920000
66	1522.74110000	20.44510000
67	1529.57260000	15.16980000
68	1542.22920000	136.02860000
69	1546.50160000	56.25610000
70	1640.00490000	13.02540000
71	1858.49970000	282.70140000
72	2746.29170000	6.49250000
73	3070.66200000	4.56330000
74	3093.58150000	0.92250000
75	3096.54340000	2.44600000
76	3100.68600000	8.18460000
77	3123.52350000	5.62900000
78	3136.07720000	1.34650000
79	3185.47000000	0.73060000
80	3190.26940000	1.44140000
81	3195.25360000	1.78180000
82	3214.16030000	1.77160000
83	3216.00570000	1.24040000
84	3217.46090000	3.83480000
85	3292.32910000	3.22250000
86	3684.30210000	120.82460000
87	3795.83830000	164.32630000

S12. ERGOTHIONINE $(1+H)_S$ (THIONE; ISOMER A) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.69200440	a.u.
Gibbs Energy	: -1065.47299100	a.u.
Number of imaginary frequencies	: 0	

S12.1. Cartesian Co-ordinates (XYZ format)

31

C	1.67734504	0.27213901	1.72266102
C	0.93941700	-0.44834200	0.84693402
C	3.06022692	-0.32745901	0.03324900
N	2.96062112	0.34002101	1.21243095
H	1.40253401	0.73387200	2.65205407
N	1.80453396	-0.80809897	-0.18105701
S	4.42213392	-0.52221102	-0.94193602
C	-0.48903799	-0.85186100	0.89861798
H	-0.90622503	-0.56134701	1.85944295
H	-0.54977500	-1.94164801	0.85933799
C	-1.41113400	-0.36568099	-0.24457701
H	-0.99581897	-0.64600003	-1.20726001
N	-1.63371003	1.14553499	-0.33694300
C	-2.72951388	-1.11765099	-0.05958400
O	-3.62653494	-0.77802497	0.66772801
O	-2.70623112	-2.24518108	-0.76744699
C	-0.40095600	1.80012596	-0.90649903
H	0.42480499	1.66882706	-0.22130300
H	-0.17851700	1.35087502	-1.86806905
H	-0.61624497	2.85595798	-1.02804005

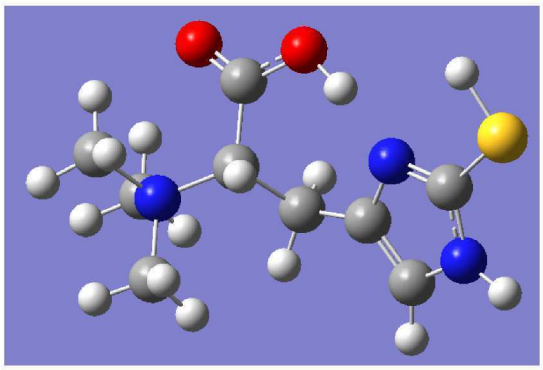
C	-1.94659305	1.77692401	0.99189001
H	-2.79836297	1.27070200	1.42725801
H	-1.07749796	1.70125401	1.63323295
H	-2.17334294	2.82194996	0.81040603
C	-2.76669097	1.42634499	-1.29361200
H	-2.79700303	2.49625397	-1.46439695
H	-2.57277107	0.90704298	-2.22674203
H	-3.69730496	1.09433103	-0.85299599
H	-3.50774407	-2.75871611	-0.57323998
H	3.74141097	0.80729699	1.64112401
H	1.58368003	-1.38242400	-0.97720802

S12.2. Frequencies

Mode	IR frequency	IR intensity
1	23.32660000	8.77510000
2	39.90990000	9.86320000
3	58.91860000	0.74140000
4	79.66510000	5.77450000
5	98.92820000	1.70670000
6	164.09240000	2.47890000
7	172.95770000	3.73270000
8	212.25690000	2.12670000
9	238.67330000	1.52420000
10	257.33550000	1.63050000
11	272.63370000	0.59100000
12	284.82960000	0.21910000
13	305.04380000	3.40630000
14	324.92270000	2.41320000
15	342.48390000	8.11620000
16	350.44650000	4.14210000
17	395.50450000	1.42660000
18	418.98330000	1.50710000
19	432.88120000	1.35600000
20	474.31610000	6.91720000
21	507.01610000	37.94420000
22	554.07790000	9.88930000
23	568.64040000	12.94580000
24	595.46740000	137.67370000
25	616.04630000	175.87650000
26	650.48760000	71.64680000
27	658.65820000	67.64190000
28	692.06680000	19.48840000
29	713.66400000	13.22120000
30	746.80240000	2.76250000
31	805.55440000	15.59470000
32	811.77120000	71.17430000
33	856.96890000	24.82990000
34	913.57930000	28.15310000
35	939.99320000	39.23590000
36	968.95540000	30.10420000
37	995.43180000	5.02810000
38	1009.66950000	34.55440000
39	1018.70840000	30.98490000
40	1049.79400000	0.88850000
41	1083.46350000	0.11650000
42	1107.28240000	72.50660000
43	1138.57800000	86.01020000
44	1151.72970000	36.81440000
45	1164.05810000	198.51900000
46	1187.22020000	210.53040000
47	1222.20830000	10.81340000

48	1259.14720000	15.15630000
49	1263.60350000	3.03060000
50	1278.41520000	10.81300000
51	1289.63740000	25.99310000
52	1297.12310000	2.16950000
53	1315.91270000	13.26500000
54	1369.60950000	74.75460000
55	1388.09270000	57.66390000
56	1407.67800000	11.26280000
57	1426.69580000	70.50430000
58	1437.69270000	15.48220000
59	1450.12930000	13.59120000
60	1455.22220000	2.55810000
61	1472.54590000	36.95010000
62	1484.51950000	6.42720000
63	1493.54730000	63.83500000
64	1495.24420000	58.76290000
65	1497.29590000	2.40850000
66	1506.14680000	414.65350000
67	1510.40510000	208.76400000
68	1515.81640000	52.48410000
69	1531.78090000	64.43780000
70	1673.73400000	51.77200000
71	1796.90490000	473.68460000
72	3046.74500000	8.13150000
73	3091.22630000	2.03140000
74	3096.00670000	6.95410000
75	3099.46370000	8.87400000
76	3114.86600000	0.44640000
77	3129.00440000	1.77410000
78	3176.97940000	0.71240000
79	3182.38130000	4.27640000
80	3184.84310000	3.75010000
81	3203.74330000	0.55510000
82	3206.59100000	2.77850000
83	3210.48570000	3.43030000
84	3289.88340000	10.03990000
85	3644.34000000	189.28100000
86	3650.95050000	132.46840000
87	3709.08410000	183.37470000

S13. ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER B) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.68262465	a.u.
Gibbs Energy	: -1065.46748400	a.u.
Number of imaginary frequencies	: 0	

S13.1. Cartesian Co-ordinates (XYZ format)

31

C	1.77723598	-1.96489501	-0.61329401
C	0.94777000	-0.88576102	-0.62099200
C	2.88488603	-0.15941601	0.03502300
N	3.00629306	-1.48624802	-0.19991900
H	1.61894095	-2.99934912	-0.85341698
N	1.65008795	0.23476800	-0.21145400
S	4.22656918	0.82625502	0.59155601
C	-0.49940401	-0.77987701	-0.97501701
H	-0.91011900	-1.78213000	-1.02541196
H	-0.62120998	-0.34825000	-1.96917605
C	-1.26206994	0.08879000	0.05999100
H	-0.72545898	0.05949500	1.00523198
N	-2.64599800	-0.45826900	0.40594599
C	-1.28849304	1.55621397	-0.41307899
O	-2.29791498	2.13948894	-0.73884100
O	-0.10687200	2.12928391	-0.45776799
C	-2.48522496	-1.80274999	1.06499302
H	-2.05934095	-2.51296806	0.36888799
H	-1.84249103	-1.69200599	1.93220901
H	-3.46963692	-2.14080405	1.36859906
C	-3.52951097	-0.60689998	-0.80224299
H	-3.65678310	0.36682400	-1.25526404
H	-3.06862211	-1.29926705	-1.49707401
H	-4.48134804	-1.00467896	-0.46703100
C	-3.32266212	0.43907899	1.41358399
H	-4.23737001	-0.05092200	1.72806096
H	-2.65753698	0.56346798	2.26219392

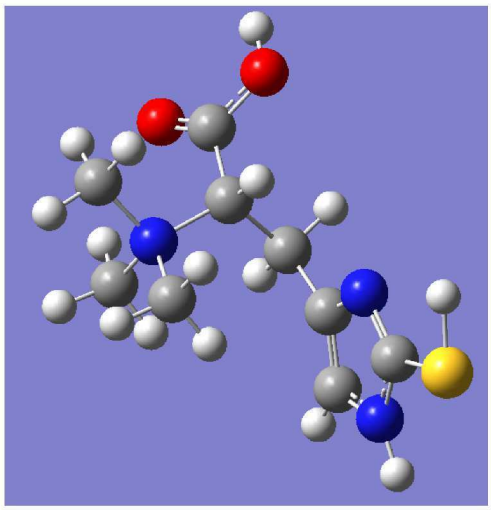
H	-3.53813791	1.39012897	0.94952297
H	3.50047493	1.95560801	0.64227200
H	0.67496598	1.49088395	-0.26792100
H	3.84249997	-2.03507495	-0.08435900

S13.2. Frequencies

Mode	IR frequency	IR intensity
1	36.38580000	1.50910000
2	53.69690000	1.49760000
3	92.77390000	4.76690000
4	99.93550000	20.82400000
5	108.87200000	10.18700000
6	122.24240000	3.51190000
7	170.38110000	12.67480000
8	199.15420000	4.06030000
9	228.45580000	6.07250000
10	251.43370000	19.42710000
11	259.37280000	15.55290000
12	260.74440000	1.36700000
13	281.79000000	4.20570000
14	306.36670000	15.82900000
15	329.31890000	7.13120000
16	337.84610000	18.13820000
17	367.47570000	11.63080000
18	387.35120000	8.10070000
19	429.12340000	2.92410000
20	440.15860000	2.43660000
21	472.75070000	2.59600000
22	495.57830000	2.01930000
23	559.86120000	6.70720000
24	576.27920000	131.09200000
25	646.76780000	4.30680000
26	676.96160000	17.78710000
27	700.87250000	1.56660000
28	737.48800000	1.41000000
29	764.16780000	15.00750000
30	784.46030000	30.99300000
31	815.00240000	33.63050000
32	855.71350000	12.80620000
33	914.39850000	61.32640000
34	926.25510000	43.26860000
35	944.76680000	29.95540000
36	974.74170000	29.87510000
37	1005.88520000	16.17330000
38	1019.89760000	23.08570000
39	1030.17920000	33.74220000
40	1039.51810000	16.18240000
41	1053.10960000	83.54170000
42	1080.46770000	0.31850000
43	1114.91830000	73.15370000
44	1144.10030000	7.02580000
45	1153.14700000	4.21970000
46	1210.82230000	13.29880000
47	1237.81680000	105.25800000
48	1243.25840000	35.12080000
49	1254.08470000	98.14110000
50	1276.18350000	81.57200000
51	1297.04310000	1.58730000
52	1299.80500000	10.16110000
53	1330.90850000	13.40190000
54	1353.38980000	40.02570000

55	1371.77730000	26.60860000
56	1421.15520000	18.97410000
57	1444.71390000	7.35920000
58	1449.75300000	32.80550000
59	1456.94680000	134.35670000
60	1476.98760000	2.90090000
61	1486.94360000	23.60960000
62	1488.48540000	5.39620000
63	1493.03710000	11.71310000
64	1501.94140000	9.10150000
65	1505.75530000	27.67830000
66	1512.78640000	138.88820000
67	1522.97350000	36.97440000
68	1527.22960000	460.76330000
69	1533.29170000	17.33830000
70	1623.88230000	95.18250000
71	1779.69490000	679.24800000
72	2575.31670000	3346.01990000
73	2696.24750000	6.48800000
74	3054.49800000	15.14540000
75	3090.79740000	10.33160000
76	3093.74000000	2.22640000
77	3097.89570000	9.66350000
78	3102.77310000	1.64140000
79	3143.12900000	6.37870000
80	3173.84930000	2.85180000
81	3178.79070000	1.43010000
82	3180.51050000	7.82190000
83	3201.76910000	4.34070000
84	3208.07450000	1.85560000
85	3220.67200000	4.17820000
86	3284.64130000	4.32950000
87	3635.71000000	167.06360000

S14. ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER C) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.67427588	a.u.
Gibbs Energy	: -1065.46237700	a.u.
Number of imaginary frequencies	: 0	

S14.1. Cartesian Co-ordinates (XYZ format)

31

C	1.68234801	0.05719300	1.90265405
C	0.91625398	-0.49878800	0.91950703
C	2.87178397	-0.23481300	0.06559600
N	2.93457198	0.22029001	1.34438896
H	1.46521401	0.34527901	2.91444397
N	1.66850495	-0.67878199	-0.22711299
S	4.27105522	-0.19420700	-1.00267506
C	-0.51906699	-0.89649898	0.96001202
H	-0.97103798	-0.62921500	1.91218996
H	-0.58530003	-1.98399198	0.88622302
C	-1.36697400	-0.37140399	-0.21595800
H	-0.82794303	-0.55633599	-1.14020801
N	-1.65114701	1.13353896	-0.21386200
C	-2.65474105	-1.18833899	-0.23145700
O	-3.66562295	-0.92456400	0.36867300
O	-2.47552800	-2.29183197	-0.95883501
C	-0.39072600	1.88887298	-0.54964399
H	0.33929399	1.72942197	0.23148000
H	-0.01116700	1.53243399	-1.50058401
H	-0.64859098	2.94026303	-0.61409301
C	-2.16811609	1.63402498	1.10652494
H	-3.03998303	1.05543697	1.38225198

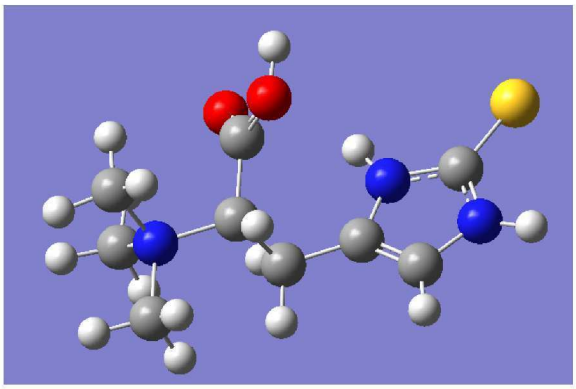
H	-1.38586199	1.54071105	1.85023201
H	-2.42681503	2.67983294	0.97916502
C	-2.65613103	1.44901800	-1.29184496
H	-2.72532296	2.52751994	-1.37833703
H	-2.30326104	1.02335000	-2.22579598
H	-3.61748290	1.03589594	-1.01692295
H	-3.26867199	-2.84752393	-0.88662899
H	3.61677003	-0.76970798	-2.02512598
H	3.74252796	0.60123599	1.80843103

S14.2. Frequencies

Mode	IR frequency	IR intensity
1	6.67270000	1.62130000
2	33.99080000	5.15880000
3	52.10500000	3.26330000
4	71.00450000	3.99500000
5	85.50940000	1.00600000
6	115.52170000	34.44910000
7	173.83300000	1.06310000
8	178.33560000	26.15980000
9	206.14450000	4.64700000
10	229.05840000	4.35160000
11	259.46600000	2.39100000
12	271.31960000	0.60720000
13	295.04900000	2.65800000
14	300.27530000	0.99480000
15	317.39510000	4.76110000
16	343.07600000	7.68300000
17	361.44420000	10.66320000
18	387.86290000	13.87040000
19	425.13320000	1.35180000
20	433.36540000	2.69660000
21	469.96440000	1.87480000
22	481.40020000	2.76420000
23	552.86170000	132.08380000
24	561.10390000	7.36350000
25	593.38780000	139.90720000
26	656.05030000	28.90700000
27	659.85260000	56.50580000
28	699.11180000	11.80980000
29	723.22230000	8.00370000
30	751.77060000	8.13130000
31	781.52330000	40.09670000
32	802.01230000	17.34780000
33	860.54970000	31.01350000
34	903.51660000	18.81290000
35	914.91380000	43.18170000
36	945.85030000	37.06220000
37	969.25450000	28.47110000
38	995.36170000	8.57850000
39	1010.57180000	58.47950000
40	1021.18250000	13.46410000
41	1051.37450000	1.95400000
42	1082.88940000	0.20220000
43	1105.66620000	53.63120000
44	1136.81730000	99.44920000
45	1145.75860000	71.17020000
46	1161.97860000	156.88480000
47	1199.22040000	18.28220000
48	1235.52150000	26.26790000
49	1256.35560000	16.83690000

50	1275.95940000	3.99140000
51	1291.55840000	12.40510000
52	1295.71530000	2.11020000
53	1302.40530000	7.23560000
54	1340.43290000	69.27420000
55	1358.18780000	71.09560000
56	1385.35570000	33.80040000
57	1430.96100000	24.16600000
58	1440.80420000	69.23700000
59	1448.33160000	21.83190000
60	1453.02290000	0.90480000
61	1469.78260000	18.99180000
62	1481.20570000	4.37730000
63	1491.17620000	29.20600000
64	1493.48420000	10.95020000
65	1498.08790000	5.37120000
66	1506.79790000	171.02830000
67	1509.40820000	25.92380000
68	1514.60160000	31.31140000
69	1531.03740000	79.77860000
70	1610.97790000	14.37520000
71	1792.46330000	477.79280000
72	2694.99630000	5.32770000
73	3046.44910000	11.78740000
74	3087.94820000	0.48500000
75	3089.45860000	8.10020000
76	3096.83030000	11.72750000
77	3111.74070000	6.71800000
78	3127.43220000	1.87390000
79	3174.16190000	0.40540000
80	3176.06210000	3.24540000
81	3181.73930000	7.04120000
82	3200.13830000	0.36240000
83	3204.26060000	4.99310000
84	3206.58280000	1.26440000
85	3277.30970000	1.98760000
86	3638.46930000	154.04730000
87	3713.98600000	171.64060000

S15. ERGOTHIONINE $(1+H)_S$ (THIONE; ISOMER A2) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.69293219	a.u.
Gibbs Energy	: -1065.47507400	a.u.
Number of imaginary frequencies	: 0	

S15.1. Cartesian Co-ordinates (XYZ format)

31

C	1.58926594	1.91456103	-0.52852499
C	0.88791603	1.07364202	0.26488400
C	3.02632308	0.30695400	0.16197000
N	2.88495994	1.43548298	-0.58086598
H	3.64781189	1.85277498	-1.08637595
H	1.27984202	2.79896808	-1.05227697
N	1.78648198	0.09279500	0.67621601
S	4.41970110	-0.61728102	0.39823100
C	-0.55199802	1.07087004	0.64658898
H	-0.91987997	2.09106898	0.59230101
H	-0.65597802	0.72816700	1.67376304
C	-1.37124896	0.17244799	-0.29599500
H	-1.29772604	0.54552799	-1.31206501
N	-2.87153292	0.16480200	0.01460200
C	-0.80878597	-1.25061405	-0.25601199
O	-0.40818301	-1.64341295	-1.46087098
O	-0.70369202	-1.90058100	0.75389600
C	-3.44441795	1.51487303	-0.32189101
H	-3.00178599	2.26673007	0.31898299
H	-3.23881197	1.73119104	-1.36489403
H	-4.51441479	1.47467101	-0.15063700
C	-3.17629790	-0.15363801	1.45420396
H	-2.68968606	-1.08380699	1.71948504
H	-2.82452893	0.65599501	2.08180499
H	-4.25293398	-0.24600200	1.54664195
C	-3.54569101	-0.85779899	-0.86134797

H	-4.61729717	-0.75869900	-0.73079097
H	-3.27521205	-0.66913801	-1.89446604
H	-3.23183608	-1.85034001	-0.55721003
H	1.58333600	-0.67589700	1.29381800
H	-0.01303600	-2.52908492	-1.39406300

S15.2. Frequencies

Mode	IR frequency	IR intensity
1	19.17870000	1.12830000
2	34.67190000	7.05010000
3	45.05830000	0.35360000
4	65.60720000	1.27660000
5	81.14020000	0.90460000
6	161.58650000	6.85710000
7	178.76640000	1.02230000
8	196.77520000	2.94800000
9	212.09080000	1.31890000
10	236.09610000	3.96560000
11	255.50710000	0.88840000
12	283.88320000	3.92030000
13	289.88460000	0.46690000
14	321.28180000	1.22820000
15	341.77450000	5.68830000
16	346.28940000	2.74620000
17	394.42610000	3.78990000
18	428.58460000	1.43060000
19	438.50800000	4.34070000
20	463.41610000	0.77160000
21	510.37120000	45.69880000
22	540.33110000	13.47220000
23	569.38480000	8.10630000
24	621.97230000	246.21820000
25	625.93780000	47.05410000
26	655.70630000	102.10030000
27	663.95070000	6.99680000
28	699.22300000	16.61960000
29	717.54110000	49.24000000
30	748.76150000	50.04920000
31	803.26680000	33.95570000
32	817.85060000	28.62090000
33	835.46550000	33.52740000
34	916.56420000	24.55640000
35	955.26410000	30.98070000
36	969.80750000	24.61380000
37	994.88770000	5.69270000
38	1002.65720000	18.93790000
39	1032.75280000	1.05720000
40	1059.22390000	3.39630000
41	1082.56160000	0.06910000
42	1106.56090000	62.73140000
43	1141.03120000	48.90680000
44	1156.76200000	15.44490000
45	1164.74770000	251.17280000
46	1182.45910000	146.10070000
47	1209.37250000	36.75980000
48	1247.93490000	4.77640000
49	1267.46400000	4.63940000
50	1269.56750000	23.02210000
51	1291.83720000	10.00160000
52	1299.02600000	25.25620000
53	1324.59320000	18.34280000

54	1362.03430000	5.48860000
55	1386.59740000	16.08290000
56	1402.86950000	34.03080000
57	1433.17940000	9.17520000
58	1438.98830000	29.04090000
59	1453.78280000	4.58490000
60	1457.01130000	12.82600000
61	1479.23100000	1.58570000
62	1484.29410000	43.21060000
63	1485.91800000	4.97350000
64	1493.64080000	34.38160000
65	1497.88020000	11.79530000
66	1505.09860000	669.33000000
67	1511.39000000	36.23410000
68	1514.29290000	44.79850000
69	1525.85110000	71.45260000
70	1671.68910000	71.87880000
71	1789.13980000	405.75220000
72	3084.73710000	5.65770000
73	3088.36110000	3.62780000
74	3094.43210000	2.69130000
75	3100.52780000	6.40630000
76	3131.58980000	0.32140000
77	3143.31960000	1.72600000
78	3180.11430000	0.60620000
79	3182.38320000	2.47940000
80	3184.80630000	3.09680000
81	3188.09820000	1.79320000
82	3195.89890000	2.33780000
83	3204.40040000	2.06310000
84	3288.64780000	8.45090000
85	3637.27550000	179.77330000
86	3651.76520000	150.21830000
87	3701.55620000	165.05550000

S16. ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ZWITTERION) IN MEOH

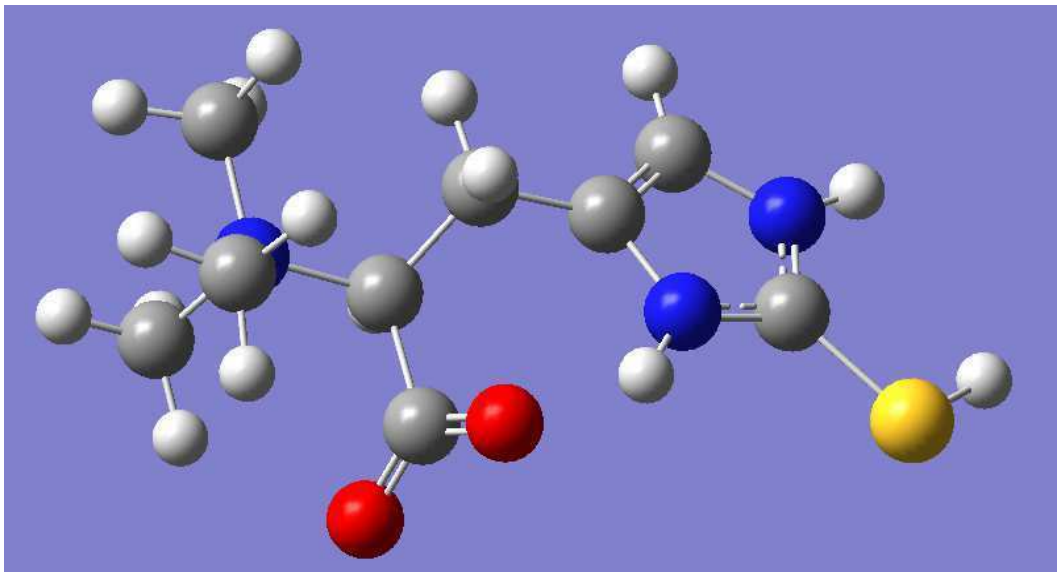


FIG. S4. Molecule

Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH+]c([nH]1)S)C(=O)[O]	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.67674224	a.u.
Gibbs Energy	: -1065.46230200	a.u.
Number of imaginary frequencies	: 0	

S16.1. Cartesian Co-ordinates (XYZ format)

31

C	1.68834901	1.99233603	-0.55695701
C	0.91517299	1.10114801	0.11189300
C	2.99925208	0.30960599	0.08850200
N	2.97660208	1.48407304	-0.55596101
H	3.77802801	1.93322897	-0.96909702
H	1.45121598	2.93122792	-1.01905501
N	1.75664699	0.07252100	0.50324702
S	4.34872007	-0.75056899	0.38022599
C	-0.53183597	1.12868798	0.46769601
H	-0.89300102	2.11113095	0.18124300
H	-0.62799001	1.03237796	1.54833102
C	-1.33702004	0.02682900	-0.23095600
H	-1.23564506	0.13162100	-1.30814803
N	-2.85416698	0.17636199	0.02651000
C	-0.88507599	-1.43106198	0.16817699
O	-1.27117503	-2.34364605	-0.57458502
O	-0.17559101	-1.52484000	1.20482695

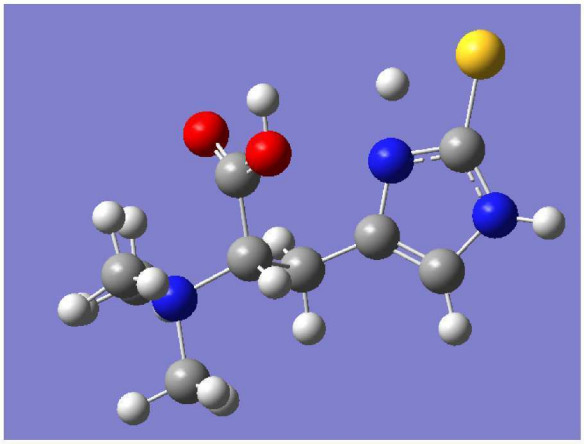
C	-3.29873610	1.60650301	-0.08741400
H	-2.92441702	2.17840505	0.75243598
H	-2.93641496	2.01512599	-1.02490199
H	-4.38346481	1.61634803	-0.07472300
C	-3.22303295	-0.33343399	1.38934803
H	-3.03280091	-1.39937603	1.42950296
H	-2.63183594	0.18281101	2.13679004
H	-4.27793121	-0.13654600	1.54902196
C	-3.61546206	-0.60753798	-1.01098800
H	-4.67072010	-0.54272300	-0.76766998
H	-3.42595196	-0.15784000	-1.98037302
H	-3.26162505	-1.62942803	-0.99649298
H	1.34310400	-0.76054901	0.95618403
H	5.21700287	-0.05033200	-0.37130600

S16.2. Frequencies

Mode	IR frequency	IR intensity
1	14.48480000	6.93150000
2	42.85520000	1.27210000
3	60.33660000	11.33640000
4	79.35020000	2.90940000
5	106.80560000	28.34520000
6	126.26380000	5.44390000
7	180.56270000	9.14440000
8	203.41540000	7.94510000
9	235.29690000	31.71310000
10	242.68380000	28.02450000
11	261.24240000	23.71500000
12	273.63050000	21.34300000
13	286.06200000	7.96920000
14	323.06580000	4.23810000
15	325.62900000	3.35320000
16	347.84390000	0.60710000
17	362.26750000	15.31830000
18	385.02410000	16.74870000
19	431.44500000	1.05860000
20	438.52930000	4.14200000
21	483.74580000	8.29270000
22	521.60120000	1.34590000
23	544.69730000	12.53180000
24	624.86640000	116.54410000
25	627.26780000	13.06250000
26	656.81420000	0.78770000
27	697.87620000	1.66600000
28	719.26550000	3.68540000
29	762.49830000	61.47010000
30	805.51480000	17.98510000
31	826.83410000	55.41360000
32	835.43540000	39.23080000
33	907.40770000	84.21000000
34	910.02440000	231.64640000
35	955.56700000	47.42070000
36	958.34720000	30.27920000
37	965.77470000	4.22300000
38	992.98540000	16.10020000
39	999.75070000	75.33680000
40	1044.18690000	2.45980000
41	1078.85600000	9.24710000
42	1086.12490000	0.29910000
43	1113.43590000	28.85770000
44	1144.28630000	3.58370000
45	1158.10540000	3.79500000
46	1193.57780000	165.64300000
47	1211.29750000	12.94430000
48	1247.20360000	1.45400000
49	1268.20430000	0.69310000
50	1288.32540000	48.75500000
51	1288.79080000	20.31240000
52	1314.10770000	30.20570000
53	1336.51780000	159.91350000
54	1353.38710000	18.22750000
55	1378.44870000	104.02620000
56	1408.78030000	11.45710000
57	1427.42700000	139.52040000
58	1448.35200000	15.62660000
59	1456.93240000	3.99780000
60	1471.10750000	19.35910000

61	1481.53440000	6.01280000
62	1484.45630000	10.27420000
63	1489.25170000	40.71600000
64	1491.41860000	6.85010000
65	1501.38420000	10.08760000
66	1505.66720000	34.57150000
67	1514.02030000	23.65450000
68	1530.44290000	16.76210000
69	1530.78100000	260.46730000
70	1656.91460000	387.53940000
71	1688.86890000	482.08590000
72	2686.42370000	13.46680000
73	3073.83210000	7.51020000
74	3085.13750000	20.23270000
75	3088.47980000	7.47520000
76	3092.96580000	8.17590000
77	3107.90830000	6.43090000
78	3137.41200000	5.19270000
79	3163.32860000	1349.17950000
80	3171.63750000	2.09400000
81	3173.46140000	11.69250000
82	3179.18300000	3.48150000
83	3190.27410000	7.37210000
84	3190.56610000	0.52010000
85	3200.30650000	8.92430000
86	3295.55470000	13.63500000
87	3635.99530000	202.74870000

S17. TRANSITION STATE BETWEEN ERGOTHIONINE $(1+H)_S$ (THIONE; ISOMER A2) AND INTERMEDIATE ERGOTHIONINE $(1N\varepsilon+H)_{SH}$ (THIOL; ISOMER C3) IN MEOH



Route	: # opt=(calcfc,ts,noeigen) freq b3lyp/cc-pvtz scrf=(iefpcm,solvent=meth	
	: anol) geom=connectivity empiricaldispersion=gd3bj int=ultrafine pop=re	
	: gular	
SMILES	: [H].C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.62246946	a.u.
Gibbs Energy	: -1065.41140500	a.u.
Number of imaginary frequencies	: 1	

S17.1. Cartesian Co-ordinates (XYZ format)

31

C	1.60383105	2.07639790	-0.35061899
C	0.92661601	1.08379495	0.29497299
C	2.99271011	0.38839301	-0.02488300
N	2.90555310	1.62274599	-0.54265600
H	3.64973402	2.13578010	-0.98433602
H	1.28647995	3.04790211	-0.68199599
N	1.81579804	0.03587700	0.48987600
S	4.11438417	-0.91469502	0.20361200
C	-0.50082397	1.02324796	0.71568203
H	-0.89694101	2.03422499	0.74144101
H	-0.56419301	0.60268402	1.71736300
C	-1.32300401	0.16423200	-0.26034999
H	-1.22076905	0.55739999	-1.26646197
N	-2.82941389	0.19120300	0.02187800
C	-0.79981899	-1.27353096	-0.23913100
O	-0.23406900	-1.58901405	-1.40200198
O	-0.86837798	-2.00475693	0.71537900
C	-3.36658907	1.54851699	-0.34150600
H	-2.91327691	2.30029607	0.29193699
H	-3.14461589	1.74334800	-1.38538802
H	-4.43923903	1.53568196	-0.18176500
C	-3.16778898	-0.10011400	1.45927000

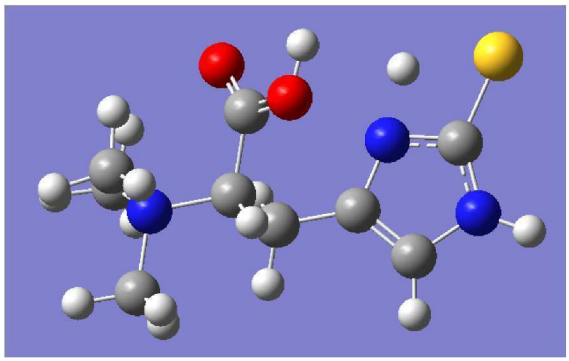
H	-2.71991992	-1.04500699	1.73909605
H	-2.79373407	0.70238400	2.08326197
H	-4.24852896	-0.14874899	1.53525996
C	-3.51196289	-0.82421601	-0.85561001
H	-4.58314896	-0.69643098	-0.74843103
H	-3.21623206	-0.65294200	-1.88511300
H	-3.22841501	-1.81979895	-0.53436702
H	0.14450499	-2.48152089	-1.33704400
H	2.51877308	-1.10883605	0.77841502

S17.2. Frequencies

Mode	IR frequency	IR intensity
1	-1739.56470000	3739.82080000
2	10.62380000	0.93010000
3	46.90570000	0.96650000
4	60.21690000	1.79770000
5	72.11740000	4.32820000
6	84.64070000	3.76770000
7	161.27610000	2.28490000
8	174.25210000	6.37270000
9	188.12950000	2.52240000
10	212.89370000	0.78740000
11	239.32040000	4.35900000
12	267.68500000	0.49250000
13	281.47750000	1.27170000
14	298.17110000	1.29350000
15	314.67200000	1.51000000
16	331.15460000	6.45750000
17	344.40340000	3.96690000
18	416.31720000	9.87240000
19	431.56550000	1.34230000
20	437.50640000	12.95470000
21	466.81250000	2.20410000
22	525.63260000	16.62750000
23	557.52620000	5.38090000
24	580.16920000	96.15320000
25	611.41320000	156.51490000
26	635.90310000	4.17860000
27	660.31680000	47.73360000
28	691.17750000	27.48380000
29	719.51970000	38.05600000
30	752.97690000	43.33050000
31	769.73160000	11.23280000
32	818.68000000	28.72860000
33	827.38260000	40.18880000
34	834.14020000	18.37120000
35	915.44490000	38.69500000
36	955.37480000	32.48330000
37	971.70510000	33.14590000
38	996.65170000	7.91930000
39	1011.00890000	8.22010000
40	1039.57710000	2.70320000
41	1058.60960000	1.00040000
42	1082.40330000	0.09300000
43	1093.76230000	70.93090000
44	1138.66220000	63.41100000
45	1155.83810000	12.65520000
46	1160.25030000	219.67180000
47	1199.45160000	50.07090000
48	1248.00250000	0.88550000
49	1258.17090000	33.23320000

50	1265.81520000	4.82400000
51	1284.63130000	35.83830000
52	1292.95330000	0.69700000
53	1319.32610000	45.80210000
54	1349.45540000	16.12020000
55	1357.87270000	13.77740000
56	1383.94200000	30.37620000
57	1435.35380000	43.75500000
58	1449.96240000	15.16780000
59	1452.75870000	58.05470000
60	1455.92110000	8.08920000
61	1477.88240000	5.05920000
62	1484.19440000	15.20860000
63	1490.38250000	3.66810000
64	1492.58710000	16.76520000
65	1497.14120000	9.08060000
66	1499.49150000	249.53310000
67	1505.66200000	46.83990000
68	1514.15560000	45.24280000
69	1526.63400000	78.81890000
70	1613.15900000	33.21290000
71	1746.56840000	17.96290000
72	1794.81390000	429.16500000
73	3078.57040000	8.46370000
74	3088.87790000	4.29430000
75	3094.80320000	2.76200000
76	3099.15330000	9.41030000
77	3128.94700000	0.78610000
78	3140.68350000	3.51460000
79	3178.45520000	0.70370000
80	3182.23110000	3.95160000
81	3186.28660000	2.93030000
82	3186.86280000	1.48390000
83	3199.28900000	2.57610000
84	3204.43810000	2.04520000
85	3274.10610000	4.40240000
86	3648.87720000	194.58160000
87	3705.82040000	156.93360000

S18. TRANSITION STATE BETWEEN ERGOTHIONINE $(1{+}H)_S$ (THIONE; ISOMER A2) AND INTERMEDIATE ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER C3)



Route	: # opt=qst2 freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd	
	: 3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.53741181	a.u.
Gibbs Energy	: -1065.32607000	a.u.
Number of imaginary frequencies	: 1	

S18.1. Cartesian Co-ordinates (XYZ format)

31

C	1.61482501	1.96945298	-0.50125998
C	0.88096702	1.07228398	0.21627600
C	2.90250611	0.21443500	-0.04645400
N	2.88521290	1.41716099	-0.65566200
H	3.66591096	1.84646201	-1.12147105
H	1.36312199	2.93667006	-0.89722699
N	1.69893396	-0.01132600	0.49216300
S	3.93374896	-1.11821401	0.26907501
C	-0.54844397	1.10458302	0.63268399
H	-0.91171700	2.12853408	0.58200002
H	-0.62299597	0.76133102	1.66378903
C	-1.39912105	0.19539601	-0.27558100
H	-1.33550799	0.54297400	-1.30277896
N	-2.90216303	0.22344799	0.05783500
C	-0.87288201	-1.24203897	-0.21133800
O	-0.25877699	-1.56410897	-1.34771895
O	-0.99901599	-1.95939398	0.74397302
C	-3.46034288	1.56398296	-0.32728001
H	-2.98248005	2.33951211	0.25914800
H	-3.28673601	1.72900701	-1.38646197
H	-4.52646208	1.55974102	-0.12231200
C	-3.19012594	-0.02406700	1.51701999
H	-2.71114612	-0.94915998	1.81440103
H	-2.81074500	0.80746102	2.09953403
H	-4.26791811	-0.08907400	1.63222599
C	-3.60778189	-0.82507098	-0.76199001

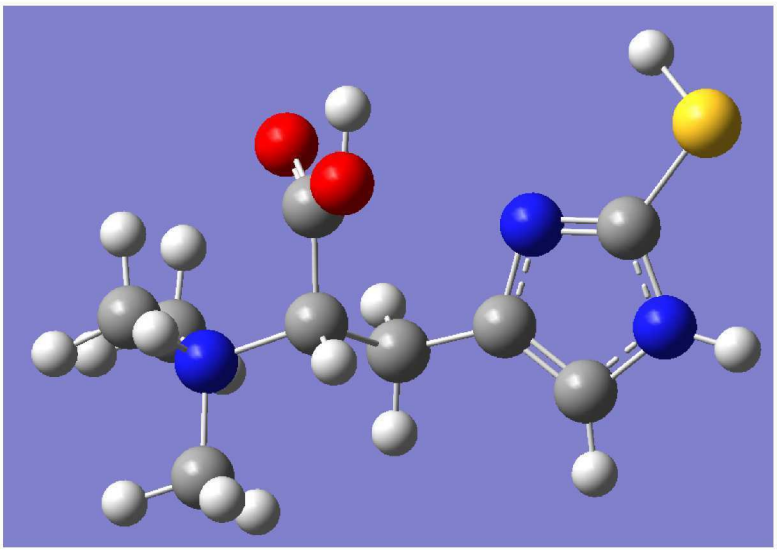
H	-4.67791414	-0.69568402	-0.63441300
H	-3.33829689	-0.69432300	-1.80604804
H	-3.31217003	-1.80764794	-0.41205701
H	0.16618700	-2.43230295	-1.24544799
H	2.29072309	-1.14064395	0.88672000

S18.2. Frequencies

Mode	IR frequency	IR intensity
1	-1693.97140000	1843.69440000
2	16.16760000	0.15980000
3	44.36410000	0.84050000
4	59.10320000	1.67610000
5	70.98880000	1.16590000
6	93.30790000	2.39990000
7	163.70720000	1.28170000
8	178.01040000	6.69550000
9	191.00260000	1.96420000
10	223.23500000	1.21230000
11	245.76670000	3.17120000
12	264.97410000	0.36950000
13	288.07610000	1.88960000
14	294.80540000	0.61140000
15	316.36770000	0.97360000
16	334.11940000	4.55420000
17	346.96010000	3.20850000
18	416.17680000	4.94360000
19	433.16160000	0.40650000
20	436.85300000	7.97740000
21	463.61290000	1.02570000
22	530.18870000	7.25220000
23	561.18230000	2.89360000
24	573.71710000	63.10900000
25	616.80210000	77.59790000
26	634.70960000	37.21810000
27	661.57740000	30.18490000
28	690.14640000	14.73900000
29	723.09630000	31.74960000
30	743.61920000	36.98440000
31	757.15170000	9.48570000
32	816.47230000	26.24170000
33	825.03940000	25.38800000
34	852.14180000	10.03530000
35	908.39580000	34.97780000
36	954.07180000	23.66780000
37	966.34630000	16.10750000
38	993.95180000	0.92970000
39	1008.11500000	2.48870000
40	1041.93020000	1.65400000
41	1050.88000000	0.28890000
42	1080.35500000	0.09100000
43	1096.31830000	38.48270000
44	1136.99730000	27.86900000
45	1151.97510000	1.12440000
46	1165.80480000	119.24980000
47	1198.23210000	40.03760000
48	1246.16690000	1.20770000
49	1260.15730000	31.04700000
50	1266.63580000	3.24240000
51	1280.28760000	44.25520000
52	1291.55790000	0.21450000
53	1317.72220000	24.82460000

54	1341.87120000	10.96540000
55	1355.36590000	16.02180000
56	1378.50850000	20.23720000
57	1430.75600000	22.36740000
58	1439.96960000	23.93770000
59	1450.07480000	14.04330000
60	1453.08510000	7.25410000
61	1478.29220000	6.90720000
62	1484.28240000	9.03720000
63	1492.07370000	9.86980000
64	1497.36410000	2.98830000
65	1500.29670000	3.57030000
66	1506.58840000	260.46020000
67	1511.44970000	25.02520000
68	1519.57840000	24.40040000
69	1534.67610000	56.26390000
70	1616.69980000	11.63060000
71	1770.09150000	7.04630000
72	1823.12410000	223.55190000
73	3066.07280000	10.42320000
74	3078.25490000	0.43890000
75	3081.60670000	0.80500000
76	3087.99090000	8.08170000
77	3112.22010000	0.82710000
78	3125.37070000	2.38100000
79	3163.62710000	0.01650000
80	3168.24610000	1.50650000
81	3173.22270000	1.61180000
82	3181.71470000	0.08550000
83	3185.46750000	1.41030000
84	3194.75300000	5.69410000
85	3263.89690000	2.88460000
86	3656.30640000	137.46920000
87	3704.19450000	117.68060000

S19. INTERMEDIATE ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER C3)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.59559793	a.u.
Gibbs Energy	: -1065.38003800	a.u.
Number of imaginary frequencies	: 1	

S19.1. Cartesian Co-ordinates (XYZ format)

31

C	2.15390396	2.52519703	-0.50584400
C	1.15781796	1.69002903	-0.08629700
C	2.92424393	0.47294801	-0.19917500
N	3.28284192	1.73536301	-0.56801897
H	4.21445990	2.04670501	-0.78621399
H	2.17528009	3.57330894	-0.74219602
N	1.64505005	0.41272199	0.09262800
S	4.08884811	-0.84308398	-0.18341500
C	-0.28212300	1.98615897	0.17403600
H	-0.44576401	3.05817294	0.08500200
H	-0.53272098	1.68092704	1.18983698
C	-1.17555904	1.22340405	-0.81455201
H	-0.87923402	1.44718599	-1.83540106
N	-2.66236210	1.63362098	-0.73968703
C	-1.05569398	-0.28681600	-0.58109599
O	-0.52335602	-0.88963503	-1.64301300
O	-1.43626904	-0.83593702	0.41698301
C	-2.81487894	3.01292300	-1.31238699
H	-2.23883510	3.71734595	-0.72471499
H	-2.46816206	3.00842309	-2.34138298

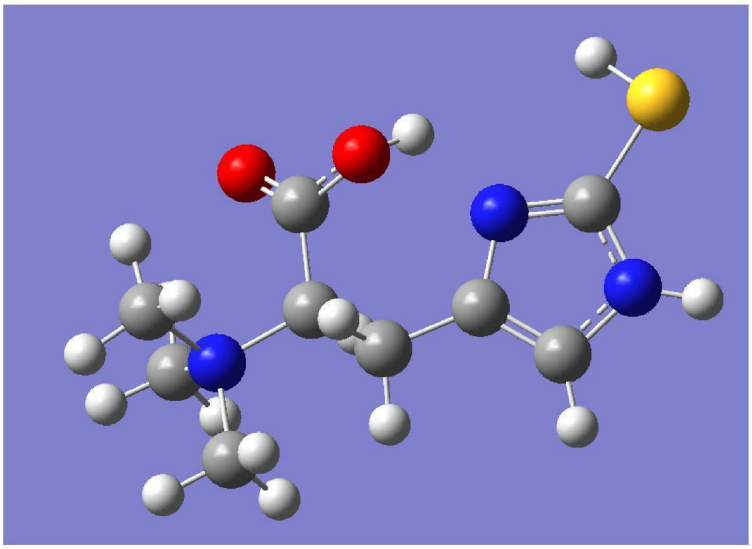
H	-3.86586404	3.28297210	-1.27556098
C	-3.20013499	1.62335706	0.66740298
H	-3.00833988	0.65089399	1.10523903
H	-2.70818996	2.40086293	1.24019599
H	-4.26602888	1.82444894	0.61471599
C	-3.48179412	0.69163299	-1.58070004
H	-4.49329090	1.08063400	-1.64313900
H	-3.04170799	0.63233000	-2.57173395
H	-3.49245691	-0.28568199	-1.11150098
H	-0.36263001	-1.82137799	-1.42237306
H	3.37467289	-1.58693194	0.67830199

S19.2. Frequencies

Mode	IR frequency	IR intensity
1	-7.21280000	0.09320000
2	48.48550000	1.54130000
3	58.85370000	1.82690000
4	75.76230000	1.39520000
5	105.72880000	19.07670000
6	114.19160000	5.39980000
7	162.17890000	3.05980000
8	188.60480000	3.13940000
9	199.73610000	8.26050000
10	223.32560000	0.84790000
11	250.87540000	4.71930000
12	259.25420000	2.58880000
13	287.84340000	3.76040000
14	293.60250000	1.92300000
15	325.05550000	1.18080000
16	333.85980000	4.67430000
17	346.34520000	2.93620000
18	372.35910000	6.55810000
19	434.17540000	0.61590000
20	438.61810000	4.12950000
21	466.53140000	0.73360000
22	478.47630000	0.44670000
23	538.88210000	7.22330000
24	560.25730000	76.70510000
25	605.72790000	89.86600000
26	656.17970000	24.40900000
27	666.84930000	10.10980000
28	710.72370000	28.61520000
29	719.03750000	28.20520000
30	757.15360000	27.33060000
31	767.30870000	7.80640000
32	816.32240000	24.05240000
33	830.12280000	25.80270000
34	900.88150000	32.67320000
35	916.21540000	16.27700000
36	956.36970000	22.46190000
37	967.42540000	13.52560000
38	993.93520000	1.51860000
39	1013.35020000	5.45150000
40	1025.94870000	2.62560000
41	1059.79370000	0.90300000
42	1080.80590000	0.07650000
43	1111.74970000	32.18690000
44	1137.22470000	27.38750000
45	1153.28140000	0.84320000
46	1164.91820000	115.94110000
47	1195.08340000	37.86170000

48	1237.03440000	26.40500000
49	1249.22610000	18.62740000
50	1267.58680000	5.89440000
51	1289.57780000	0.89000000
52	1299.44480000	2.07090000
53	1316.73150000	17.23870000
54	1345.83230000	5.13650000
55	1357.44110000	23.28010000
56	1380.38860000	9.19020000
57	1427.54390000	14.65530000
58	1439.66300000	38.87100000
59	1450.77910000	12.42150000
60	1452.98750000	7.33580000
61	1475.44250000	5.76720000
62	1483.96300000	8.09190000
63	1491.91440000	11.13820000
64	1497.57690000	0.90540000
65	1499.95120000	6.69320000
66	1510.83900000	29.98170000
67	1514.43470000	102.77940000
68	1519.73280000	29.71310000
69	1534.33990000	56.74920000
70	1606.27860000	11.97760000
71	1823.71060000	224.79180000
72	2691.14440000	3.78570000
73	3060.43390000	11.97720000
74	3078.36840000	0.58220000
75	3081.35710000	1.34350000
76	3087.13170000	8.28940000
77	3108.92990000	2.34490000
78	3122.16060000	3.42920000
79	3163.21190000	0.06010000
80	3167.98270000	1.74290000
81	3172.58070000	2.13630000
82	3180.82920000	0.15270000
83	3186.37220000	1.69680000
84	3192.55340000	4.59790000
85	3269.14300000	1.44210000
86	3641.30800000	106.17780000
87	3719.19500000	116.92040000

S20. TRANSITION STATE BETWEEN INTERMEDIATE ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER C3) AND ERGOTHIONINE $(1N\varepsilon{+}H)_{SH}$ (THIOL; ISOMER B)



Route	: # opt=(calcfc,qst3,noeigen) freq b3lyp/cc-pvtz geom=connectivity empir	
	: icaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)O	
Formula	: $C_9H_{16}N_3O_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1065.58565517	a.u.
Gibbs Energy	: -1065.37266700	a.u.
Number of imaginary frequencies	: 1	

S20.1. Cartesian Co-ordinates (XYZ format)

31

C	2.22121596	2.69492888	-0.90482098
C	1.07476699	1.99613404	-0.66097599
C	2.69804597	0.58964401	-0.41953000
N	3.24825096	1.79009104	-0.74310702
H	2.40135908	3.72568893	-1.14971006
N	1.38541996	0.67758203	-0.36416301
S	3.68690991	-0.84224898	-0.18594900
C	-0.32502800	2.52807689	-0.60873401
H	-0.73280299	2.34013796	0.38495201
H	-0.27244300	3.60571408	-0.75020897
C	-1.28510904	1.91009700	-1.65436101
H	-0.87510401	2.02495694	-2.65375090
N	-2.65410089	2.61119390	-1.70221996
C	-1.40263104	0.41929200	-1.33480096
O	-2.17558002	-0.02374700	-0.53222197
O	-0.48512101	-0.28042400	-2.01189089
C	-2.48671198	3.97088790	-2.31606889
H	-3.46498609	4.43647814	-2.38626003
H	-1.84231305	4.57788181	-1.69149303

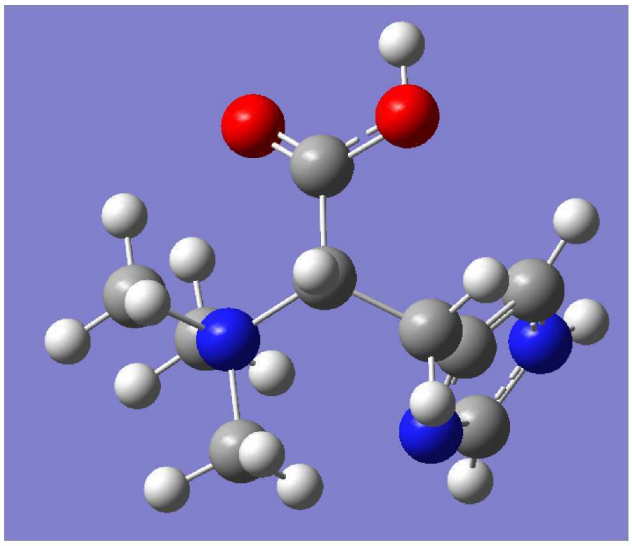
H	-2.05671811	3.86136508	-3.30715489
C	-3.29641390	2.76324511	-0.34769401
H	-4.28809404	3.17916989	-0.49901101
H	-3.35307288	1.78729904	0.11832900
H	-2.70412588	3.44426107	0.25257501
C	-3.57613301	1.81603003	-2.59064293
H	-3.80309606	0.87207401	-2.11074591
H	-4.48583984	2.38983989	-2.73754907
H	-3.08329892	1.65051901	-3.54454589
H	2.80042005	-1.44445205	0.62580597
H	0.23715501	-0.51401502	-1.38280702
H	4.23293495	1.99103200	-0.79846799

S20.2. Frequencies

Mode	IR frequency	IR intensity
1	-378.16210000	259.63560000
2	36.95800000	0.26260000
3	50.39420000	1.52150000
4	72.60590000	1.20690000
5	91.00800000	0.43390000
6	120.24410000	21.95430000
7	157.40150000	2.72060000
8	170.84690000	16.38350000
9	195.00110000	6.27740000
10	220.85590000	1.93660000
11	236.51880000	5.60030000
12	254.50310000	2.13100000
13	275.00480000	1.17830000
14	288.88540000	3.02970000
15	305.69190000	5.75010000
16	321.28680000	2.38880000
17	336.29370000	6.26360000
18	348.33290000	4.39720000
19	379.16980000	9.18470000
20	424.56740000	1.61240000
21	433.79220000	0.50010000
22	467.25420000	0.18310000
23	483.25630000	2.20850000
24	547.15800000	2.22530000
25	576.29430000	79.97660000
26	655.52870000	1.59340000
27	677.07040000	19.59810000
28	703.55740000	2.08550000
29	723.31070000	2.17480000
30	749.54190000	1.37340000
31	775.14110000	20.79100000
32	819.76490000	19.76890000
33	841.05660000	12.78370000
34	909.03040000	45.22860000
35	924.44600000	18.34350000
36	951.57260000	25.64300000
37	966.61750000	16.26360000
38	996.90690000	1.39200000
39	1013.04540000	4.02860000
40	1019.01790000	9.24000000
41	1030.74520000	3.79990000
42	1078.96440000	0.12440000
43	1116.54200000	35.14510000
44	1135.56410000	54.26290000
45	1149.31170000	1.80790000
46	1154.93460000	100.92510000

47	1192.71800000	50.65570000
48	1237.41050000	33.37110000
49	1252.45560000	33.07320000
50	1262.98040000	10.99910000
51	1287.71850000	9.00610000
52	1295.35370000	5.21150000
53	1301.07260000	21.35630000
54	1338.44150000	0.65910000
55	1352.46050000	10.41230000
56	1360.40610000	25.92230000
57	1411.54220000	13.79260000
58	1443.97010000	28.64390000
59	1446.17760000	11.98150000
60	1452.10680000	13.65460000
61	1477.29690000	4.49510000
62	1484.75520000	6.52800000
63	1491.33530000	14.63350000
64	1497.26900000	1.74840000
65	1501.94670000	3.70260000
66	1511.59660000	25.70350000
67	1514.31490000	106.67990000
68	1519.45400000	25.10080000
69	1536.28440000	56.05590000
70	1606.08340000	15.46710000
71	1816.68940000	255.78610000
72	2686.42410000	4.72320000
73	3053.95280000	9.75160000
74	3078.23290000	0.80460000
75	3081.51150000	1.16960000
76	3087.86460000	9.36960000
77	3104.55060000	3.02620000
78	3120.29840000	2.22830000
79	3161.41480000	0.17650000
80	3166.43830000	2.25200000
81	3171.35720000	2.56990000
82	3183.70040000	2.27630000
83	3191.61080000	0.07980000
84	3197.07310000	6.95340000
85	3270.31710000	2.27700000
86	3424.47550000	649.13600000
87	3639.56260000	116.30220000

S21. HERCYNINE (CONFORMER A)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.37374957	a.u.
Gibbs Energy	: -667.15464500	a.u.
Number of imaginary frequencies	: 0	

S21.1. Cartesian Co-ordinates (XYZ format)

30

C	2.49005008	0.89410597	0.14885400
C	1.54090500	-0.00742300	0.55024600
C	3.00394797	-1.13282096	-0.55782998
N	3.41367507	0.16177601	-0.55707502
H	4.25670719	0.51816100	-0.97572303
H	2.59838891	1.94989204	0.31670299
N	1.87559605	-1.26934600	0.10127500
C	0.34031799	0.21269000	1.40590501
H	0.45856899	1.13819301	1.96406305
H	0.27881801	-0.57904500	2.14882302
C	-1.03094900	0.35443699	0.71075201
H	-1.75545299	0.52727097	1.50815797
N	-1.57096696	-0.89621401	-0.00162200
C	-1.10565197	1.59881604	-0.17861700
O	-1.56148398	1.66024899	-1.28795505
O	-0.62755299	2.65439010	0.48959601
C	-1.33962905	-2.10170388	0.87082398
H	-0.27730301	-2.32130694	0.89139003
H	-1.72096896	-1.90084803	1.86801696
H	-1.88317204	-2.93219709	0.43164301

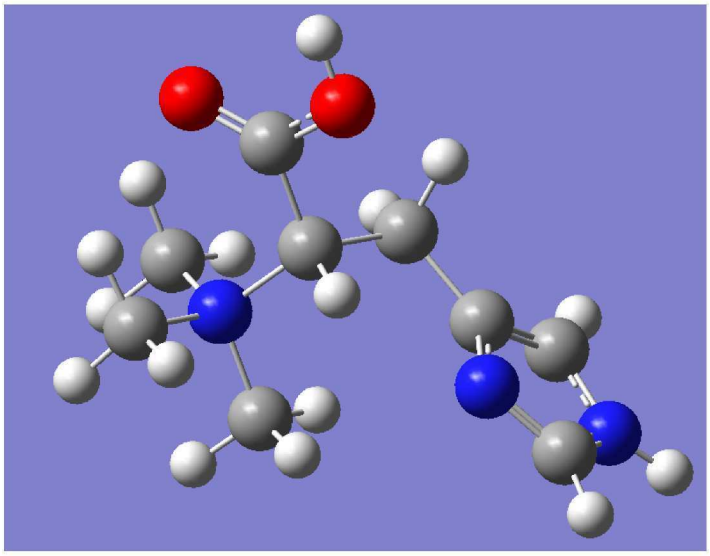
C	-0.94052702	-1.18672001	-1.34709501
H	-1.13839102	-0.36069101	-2.01462412
H	0.12010800	-1.34547603	-1.19900405
H	-1.40393102	-2.09618092	-1.71811604
C	-3.05723906	-0.73527402	-0.19280200
H	-3.43404007	-1.63429296	-0.66990203
H	-3.52452493	-0.61215299	0.78014302
H	-3.24085093	0.12599300	-0.82273901
H	-0.73658401	3.44065404	-0.06913400
H	3.55574894	-1.92114305	-1.04040694

S21.2. Frequencies

Mode	IR frequency	IR intensity
1	34.97000000	4.32480000
2	36.85970000	3.54670000
3	61.34850000	3.53610000
4	105.87800000	0.33800000
5	136.74200000	4.98510000
6	219.53900000	8.53060000
7	227.00540000	1.09710000
8	244.28180000	3.12200000
9	265.49120000	5.76910000
10	277.58420000	2.51490000
11	307.46460000	5.89010000
12	340.65600000	6.18040000
13	351.00190000	0.07980000
14	368.41060000	6.90250000
15	415.07360000	0.91210000
16	430.79370000	2.29660000
17	439.59070000	0.72760000
18	522.98680000	12.50900000
19	545.39720000	8.59920000
20	588.73110000	68.31240000
21	604.99580000	59.02330000
22	639.65470000	47.79750000
23	659.84090000	28.61530000
24	673.90750000	10.94720000
25	704.13160000	25.09280000
26	728.75460000	11.30290000
27	786.93710000	16.69000000
28	808.63770000	19.98260000
29	857.58720000	19.78900000
30	864.11600000	2.17640000
31	887.33380000	42.00030000
32	951.21030000	18.72030000
33	959.63680000	10.15370000
34	962.50330000	0.43140000
35	981.34090000	15.00750000
36	1006.47290000	18.70840000
37	1040.98810000	27.04320000
38	1085.89370000	0.52380000
39	1102.51090000	24.89110000
40	1141.52930000	16.84760000
41	1145.49720000	31.92090000
42	1150.02590000	39.10510000
43	1173.34680000	159.18320000
44	1222.54900000	4.07860000
45	1248.39430000	0.98680000
46	1258.84200000	2.39280000
47	1265.08230000	5.12730000
48	1294.71530000	1.57860000

49	1299.64280000	2.05320000
50	1319.46080000	0.63020000
51	1343.38540000	14.33270000
52	1365.78070000	3.98130000
53	1403.61360000	6.68070000
54	1415.31340000	23.81950000
55	1448.52740000	8.86810000
56	1451.88240000	4.82160000
57	1456.60010000	20.68120000
58	1481.61460000	20.00150000
59	1483.08060000	2.65170000
60	1493.90930000	14.60230000
61	1501.58840000	10.34670000
62	1507.28770000	2.62830000
63	1517.22390000	21.12500000
64	1525.15950000	0.50470000
65	1529.51320000	38.30110000
66	1545.11140000	32.57090000
67	1601.05080000	6.11100000
68	1822.11170000	242.50970000
69	3060.14010000	1.67480000
70	3069.56740000	3.75440000
71	3080.66720000	2.45890000
72	3089.22840000	17.89130000
73	3091.15140000	20.77300000
74	3126.06240000	0.99880000
75	3159.78140000	0.31670000
76	3165.18380000	6.04110000
77	3169.95590000	0.88290000
78	3175.38550000	20.43490000
79	3194.86990000	1.82150000
80	3219.23110000	15.35190000
81	3255.03130000	1.94020000
82	3272.85770000	1.72510000
83	3640.85200000	117.19070000
84	3721.09380000	144.96290000

S22. HERCYNINE (CONFORMER B)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.37248367	a.u.
Gibbs Energy	: -667.15228800	a.u.
Number of imaginary frequencies	: 1	

S22.1. Cartesian Co-ordinates (XYZ format)

30

C	-2.79852700	-0.70270097	-1.05536199
C	-1.68843305	-0.56571901	-0.26628399
C	-3.33555007	0.18616401	0.89286900
N	-3.84158897	-0.22061300	-0.29791000
H	-4.80801678	-0.18542901	-0.57689297
H	-2.94313598	-1.10268795	-2.04237008
N	-2.03589511	-0.00698100	0.94189602
C	-0.27768701	-1.00032401	-0.53241903
H	-0.03537600	-0.94656801	-1.59269595
H	-0.17766300	-2.05131292	-0.25981599
C	0.75501698	-0.24377100	0.32349399
H	0.26122800	-0.00057700	1.26383400
N	1.20435703	1.10669303	-0.24908800
C	1.94441605	-1.14624798	0.64043301
O	3.06201911	-1.04161704	0.20811500
O	1.54990304	-2.10320091	1.48362398
C	0.00605300	2.00310612	-0.41621101
H	-0.64932501	1.58893299	-1.17261398
H	-0.52499902	2.06264091	0.52714902
H	0.36597601	2.97949195	-0.72517198

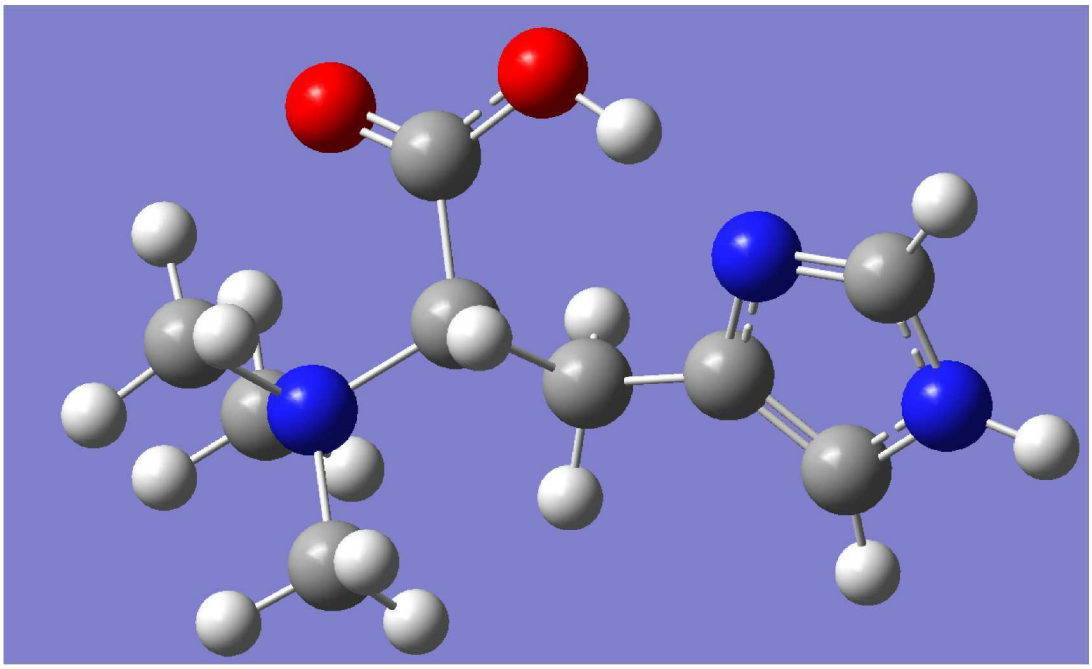
C	1.89611495	0.99319798	-1.58205700
H	2.76389599	0.35598999	-1.47633302
H	1.20172703	0.58540201	-2.30749798
H	2.18712497	1.99418497	-1.88592303
C	2.13231802	1.77570403	0.73300397
H	2.35252309	2.77213907	0.36332700
H	1.62712097	1.84132600	1.69224596
H	3.04352689	1.19751406	0.81459600
H	2.30019689	-2.69403601	1.65774906
H	-3.94265389	0.61010200	1.67411101

S22.2. Frequencies

Mode	IR frequency	IR intensity
1	-14.38230000	0.87070000
2	50.45590000	2.09980000
3	68.99260000	4.86660000
4	92.90920000	1.78070000
5	133.26550000	5.77390000
6	198.22940000	3.08070000
7	220.18250000	0.92200000
8	246.42500000	13.22300000
9	256.09430000	1.16190000
10	275.78830000	3.00060000
11	291.61220000	1.64910000
12	313.51070000	1.06930000
13	329.17150000	2.39490000
14	345.34470000	4.79220000
15	363.15120000	11.63420000
16	422.87360000	0.48780000
17	435.64800000	1.21130000
18	491.01740000	2.01070000
19	551.69420000	9.39090000
20	588.74000000	86.11550000
21	605.92850000	88.97120000
22	650.69020000	23.39000000
23	661.20920000	29.24690000
24	684.53800000	17.57670000
25	712.77170000	7.70620000
26	747.43020000	7.36600000
27	778.45390000	6.44930000
28	789.89930000	25.46360000
29	852.23820000	25.90670000
30	864.18930000	13.38030000
31	909.92600000	24.96080000
32	947.62640000	25.10280000
33	962.77210000	7.29120000
34	970.01500000	8.49910000
35	988.97100000	12.18240000
36	1010.07360000	41.49540000
37	1061.76140000	2.71380000
38	1080.30860000	0.01540000
39	1100.01960000	25.29680000
40	1137.18710000	26.18550000
41	1140.80110000	24.21840000
42	1155.47990000	11.40730000
43	1171.77950000	181.48560000
44	1212.11000000	3.75330000
45	1250.44480000	2.65500000
46	1254.57140000	29.70820000
47	1274.52160000	1.69660000
48	1290.44010000	2.52950000

49	1302.11170000	3.13340000
50	1304.96330000	2.53050000
51	1335.28320000	5.57670000
52	1361.24860000	51.48430000
53	1394.94820000	26.96930000
54	1433.38670000	14.64760000
55	1445.92410000	12.03140000
56	1455.04990000	2.23280000
57	1460.44650000	25.04620000
58	1474.96990000	7.36600000
59	1481.02430000	4.06440000
60	1491.22110000	32.95180000
61	1498.02090000	7.33490000
62	1502.08390000	1.03860000
63	1513.71410000	15.72020000
64	1518.34060000	19.28830000
65	1523.00860000	28.86660000
66	1537.45370000	58.31440000
67	1594.94100000	10.84390000
68	1816.85280000	284.31280000
69	3061.00440000	7.55430000
70	3079.05800000	18.84940000
71	3081.59840000	1.78830000
72	3085.01810000	2.86260000
73	3091.65350000	6.41240000
74	3097.88430000	6.50320000
75	3164.20720000	1.15690000
76	3170.83780000	1.31500000
77	3176.82170000	2.32710000
78	3188.29500000	1.21340000
79	3198.59530000	0.59370000
80	3206.67120000	6.40370000
81	3255.52140000	1.83180000
82	3268.99470000	1.60060000
83	3639.99530000	117.19460000
84	3721.61340000	157.31040000

S23. HERCYNINE (CONFORMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.37624043	a.u.
Gibbs Energy	: -667.15661600	a.u.
Number of imaginary frequencies	: 0	

S23.1. Cartesian Co-ordinates (XYZ format)

30

C	2.79753208	-1.26665294	-0.51397300
C	1.74280298	-0.40939301	-0.37264100
C	3.42008209	0.51801699	0.63329101
N	3.85257602	-0.65811002	0.12796099
H	2.89584899	-2.21795607	-1.00351501
N	2.14745307	0.69340199	0.34832600
C	0.33938000	-0.51221597	-0.88567400
H	0.13170700	-1.55560601	-1.10571206
H	0.23977500	0.02591500	-1.83039296
C	-0.67340797	0.06437900	0.13515900
H	-0.25911501	-0.02925900	1.13726497
N	-1.98685205	-0.72685200	0.20324200
C	-0.91309702	1.56930399	-0.15198000
O	-1.96489000	1.98371196	-0.57354099
O	0.12223800	2.33467889	0.08104600

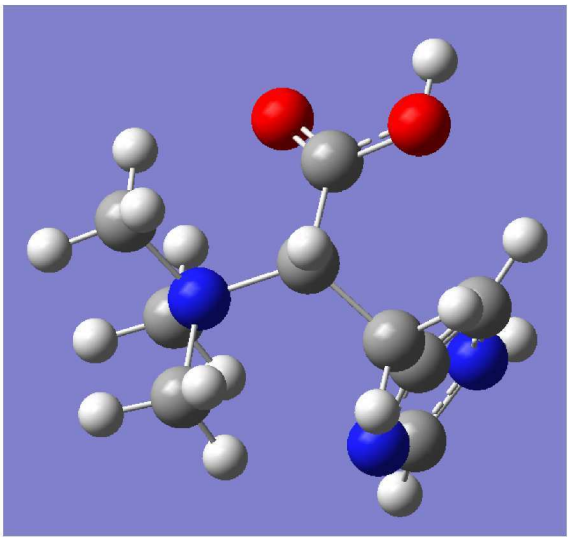
C	-1.69806099	-2.11297989	0.70587701
H	-1.07279098	-2.64583206	0.00049100
H	-1.20040596	-2.04272795	1.66850305
H	-2.64256907	-2.63638306	0.81509298
C	-2.67621899	-0.82202202	-1.13291705
H	-2.89366198	0.18140601	-1.47552299
H	-2.02566004	-1.33807194	-1.83074796
H	-3.58966899	-1.39290404	-0.99534899
C	-2.92380309	-0.08628100	1.20164001
H	-3.78125906	-0.74130398	1.31976104
H	-2.40021896	0.01177200	2.14860201
H	-3.22638297	0.88195598	0.82828802
H	0.96451998	1.82056105	0.32148200
H	4.78680801	-1.02516699	0.20690000
H	4.04574919	1.19668806	1.18590295

S23.2. Frequencies

Mode	IR frequency	IR intensity
1	44.00650000	1.52530000
2	71.24550000	0.64520000
3	90.99300000	0.99120000
4	112.54680000	2.57940000
5	167.74300000	5.06940000
6	208.09520000	3.83670000
7	229.93900000	9.43830000
8	242.48670000	3.05390000
9	260.84560000	5.39960000
10	262.73070000	6.22190000
11	281.46310000	0.76810000
12	319.58120000	7.93000000
13	328.49350000	12.55290000
14	358.43870000	3.09000000
15	369.83420000	3.68050000
16	428.35980000	1.03620000
17	439.03530000	1.00140000
18	485.15010000	1.96520000
19	552.49830000	2.79630000
20	603.76120000	89.71300000
21	655.19270000	6.14400000
22	675.90230000	12.85500000
23	683.69030000	8.19160000
24	727.47240000	0.70120000
25	761.39000000	5.29270000
26	787.89390000	10.74710000
27	811.71130000	18.95330000
28	845.94390000	6.25930000
29	860.08700000	25.87050000
30	907.27120000	44.83280000
31	944.43330000	18.22640000
32	967.82890000	11.34480000
33	971.60060000	9.00260000
34	998.29190000	12.50990000
35	1014.83520000	5.34780000
36	1025.09350000	74.63140000
37	1051.04690000	26.44270000
38	1075.59790000	0.41760000
39	1102.17430000	32.58610000
40	1138.66980000	3.16600000
41	1149.67750000	2.89600000
42	1160.40300000	10.25820000
43	1212.35860000	7.12520000

44	1241.41670000	27.18730000
45	1245.13520000	29.55300000
46	1260.45710000	22.64200000
47	1276.65590000	35.74440000
48	1295.09020000	5.75520000
49	1302.51620000	4.02870000
50	1330.33290000	23.74820000
51	1348.43330000	8.26450000
52	1377.27630000	15.51690000
53	1416.07070000	3.21240000
54	1439.72050000	7.79810000
55	1447.56840000	16.65950000
56	1471.33810000	20.65460000
57	1475.71580000	0.97590000
58	1484.15750000	32.18950000
59	1491.96580000	3.07480000
60	1496.99390000	2.38250000
61	1507.75330000	5.76820000
62	1508.21470000	22.58660000
63	1514.33270000	174.38820000
64	1524.30760000	46.24340000
65	1532.47850000	57.73500000
66	1539.28060000	46.44090000
67	1610.86680000	39.64250000
68	1813.82340000	384.11940000
69	2804.95310000	1787.61870000
70	3044.49610000	6.37460000
71	3079.29120000	2.90640000
72	3083.29260000	1.60810000
73	3086.76770000	6.85060000
74	3090.80170000	3.35800000
75	3116.47190000	7.39570000
76	3160.45830000	0.77990000
77	3166.77550000	1.74500000
78	3169.88680000	4.06310000
79	3187.95300000	3.47700000
80	3199.14050000	4.76190000
81	3209.86890000	9.67640000
82	3265.82540000	6.57050000
83	3275.41900000	3.01480000
84	3638.92670000	134.35500000

S24. HERCYNINE (CONFORMER A) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(iefpcm,solvent=methanol) geom=connectiv	
	: ity empiricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.44662452	a.u.
Gibbs Energy	: -667.22608900	a.u.
Number of imaginary frequencies	: 1	

S24.1. Cartesian Co-ordinates (XYZ format)

30

C	2.30900311	1.00717103	-0.00692600
C	1.57441401	-0.01271200	0.53988898
C	3.13773489	-0.94262600	-0.61380100
N	3.29622197	0.39759800	-0.74032003
H	4.01821089	0.86372399	-1.26448798
H	2.22697210	2.07571697	0.06742000
N	2.10695195	-1.22764504	0.15384699
C	0.37935600	0.07049100	1.43022299
H	0.47798100	0.92569703	2.09533691
H	0.34036201	-0.80538797	2.07075691
C	-0.99672401	0.27296299	0.75292403
H	-1.71150696	0.46735701	1.55019701
N	-1.57943904	-0.94053602	0.02664800
C	-0.97049701	1.52454305	-0.12136600
O	-1.13842297	1.58496594	-1.31157696
O	-0.71674103	2.58478999	0.65052700
C	-1.60730803	-2.10844898	0.97473103
H	-0.59463298	-2.44369698	1.15966201
H	-2.09022498	-1.80617905	1.89828598
H	-2.17384005	-2.90254092	0.50130498

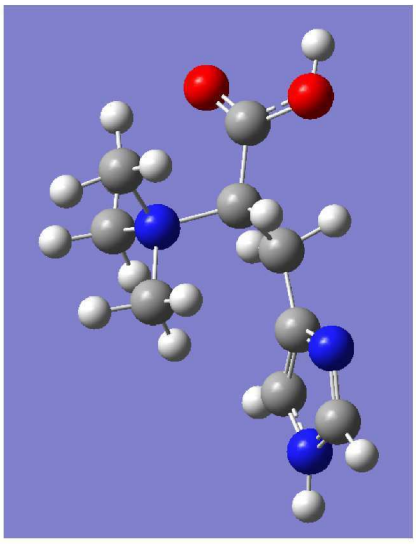
C	-0.81639302	-1.36544204	-1.20392704
H	-0.79366702	-0.54138398	-1.90251505
H	0.18383200	-1.65668404	-0.90905201
H	-1.34663701	-2.21203494	-1.62783098
C	-3.00330400	-0.63382602	-0.36094800
H	-3.42705989	-1.52626002	-0.80756301
H	-3.55724597	-0.36692700	0.53317702
H	-3.00743198	0.17864899	-1.07501197
H	-0.68406999	3.37672400	0.09020200
H	3.79073811	-1.65267503	-1.09098005

S24.2. Frequencies

Mode	IR frequency	IR intensity
1	-6.24600000	6.09280000
2	38.84960000	6.97460000
3	67.56130000	4.00950000
4	98.12530000	1.42800000
5	117.51230000	8.39410000
6	209.18690000	11.98490000
7	226.05530000	0.60950000
8	241.59530000	3.88120000
9	252.69580000	8.69920000
10	280.66770000	4.59700000
11	296.06970000	7.68700000
12	329.80450000	1.64960000
13	340.09740000	10.95920000
14	360.30090000	14.66280000
15	403.19280000	3.26820000
16	428.91520000	1.26750000
17	437.80390000	0.57300000
18	513.29660000	13.05080000
19	549.33740000	26.30590000
20	583.64980000	127.31930000
21	598.13290000	144.80620000
22	635.45420000	29.88480000
23	658.03210000	41.99090000
24	676.22070000	4.46330000
25	718.44220000	25.61100000
26	725.60780000	11.27930000
27	791.64620000	19.07730000
28	808.73110000	26.43800000
29	851.86150000	24.10780000
30	868.86650000	5.14780000
31	889.46220000	65.62150000
32	952.73400000	33.91510000
33	959.50380000	1.95010000
34	962.18690000	2.71010000
35	983.81290000	39.17460000
36	1008.01610000	33.39920000
37	1032.03520000	33.64370000
38	1086.29140000	0.83510000
39	1101.84520000	44.58100000
40	1138.74400000	208.93370000
41	1143.17930000	7.10440000
42	1154.26080000	8.71950000
43	1163.41350000	173.23230000
44	1216.74400000	17.91000000
45	1246.30930000	3.54060000
46	1260.42800000	4.79650000
47	1263.21180000	1.85360000
48	1292.35860000	1.94560000

49	1301.11570000	3.02370000
50	1318.08050000	0.42870000
51	1342.28700000	28.50920000
52	1363.92480000	10.29090000
53	1403.25620000	15.19140000
54	1427.12080000	33.03940000
55	1450.36510000	2.18380000
56	1454.31340000	11.18190000
57	1457.56400000	31.82710000
58	1473.13570000	27.37700000
59	1482.96630000	4.09980000
60	1493.01810000	6.26910000
61	1496.72250000	1.87110000
62	1500.33570000	7.05890000
63	1508.88390000	51.66990000
64	1522.84920000	8.48010000
65	1524.20700000	56.34690000
66	1535.53260000	70.32330000
67	1593.58530000	9.41850000
68	1797.07760000	430.68120000
69	3087.34960000	1.91470000
70	3090.00820000	8.53200000
71	3090.65090000	11.67020000
72	3094.02820000	25.92340000
73	3099.83760000	11.03310000
74	3134.32870000	5.34860000
75	3173.21650000	1.87840000
76	3178.25750000	11.46600000
77	3180.18400000	6.24640000
78	3193.30700000	0.69370000
79	3204.39700000	1.41900000
80	3215.79280000	12.04860000
81	3255.81530000	0.70150000
82	3275.32510000	0.96250000
83	3641.75120000	151.83230000
84	3721.69480000	177.71570000

S25. HERCYNINE (CONFORMER B) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.44640776	a.u.
Gibbs Energy	: -667.22863600	a.u.
Number of imaginary frequencies	: 0	

S25.1. Cartesian Co-ordinates (XYZ format)

30

C	-2.58108807	-0.07807300	1.25624895
C	-1.66607797	0.46631199	0.39542899
C	-3.41831589	0.05509400	-0.77876502
N	-3.69354105	-0.33352500	0.49077901
H	-4.55738592	-0.73480201	0.81621599
H	-2.54075003	-0.29973200	2.30672002
N	-2.20037794	0.54567897	-0.87315601
C	-0.28343499	0.94539601	0.68092299
H	-0.01468100	0.76788199	1.71938598
H	-0.25132200	2.02787590	0.54088998
C	0.80252099	0.39740601	-0.26674399
H	0.45364800	0.50057799	-1.28990304
N	1.13974404	-1.08889699	-0.10840000
C	2.03456807	1.27738094	-0.08193900
O	2.91412497	1.10108805	0.72249401
O	1.96216905	2.32670689	-0.90201199
C	0.00334500	-1.92641497	-0.63754398
H	-0.86884999	-1.77992105	-0.01603000
H	-0.20664699	-1.62652504	-1.65794396
H	0.31974500	-2.96338201	-0.60560799

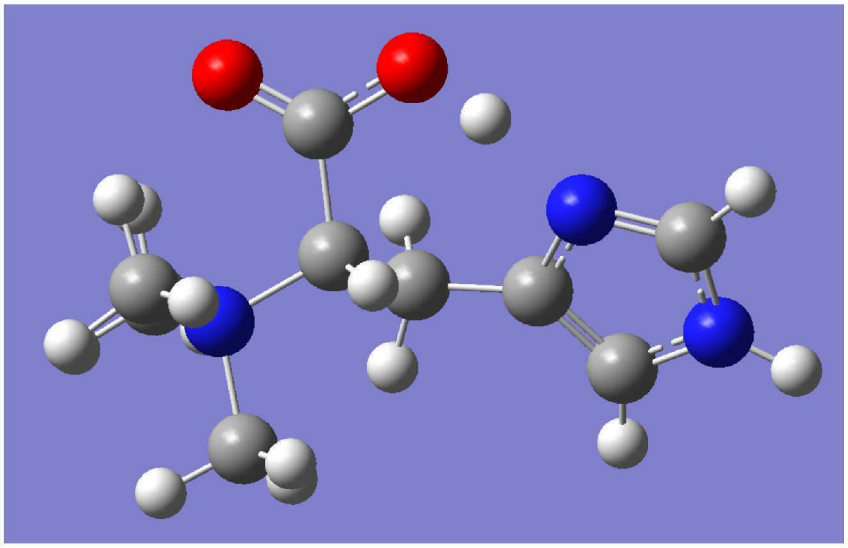
C	1.40093398	-1.48372602	1.31885302
H	2.18283701	-0.85143399	1.71855605
H	0.48513299	-1.37790799	1.88743401
H	1.71119797	-2.52296805	1.31963503
C	2.35196304	-1.41404605	-0.94288999
H	2.48250103	-2.49036789	-0.93676603
H	2.17550111	-1.06805396	-1.95631695
H	3.22110510	-0.93196303	-0.51570702
H	2.70194507	2.92611909	-0.71078402
H	-4.12967205	-0.03897200	-1.58107996

S25.2. Frequencies

Mode	IR frequency	IR intensity
1	21.18200000	1.04190000
2	51.26710000	6.28870000
3	69.24470000	5.39710000
4	74.01210000	5.36170000
5	110.30500000	6.88610000
6	179.73200000	4.33700000
7	218.39030000	2.03070000
8	242.79440000	10.72270000
9	253.59700000	2.27380000
10	281.04770000	1.52300000
11	287.64220000	5.05830000
12	309.81840000	7.32740000
13	347.31640000	8.98750000
14	352.76370000	15.35340000
15	369.30110000	6.99380000
16	419.45480000	0.63910000
17	437.78070000	1.81810000
18	479.27330000	4.84430000
19	559.55860000	13.83390000
20	577.00490000	125.19820000
21	591.62280000	159.43950000
22	655.03120000	65.91110000
23	662.27830000	7.34670000
24	683.54660000	32.30000000
25	717.86670000	9.36740000
26	752.14610000	2.73720000
27	790.20830000	27.13590000
28	800.06310000	13.53000000
29	852.68470000	45.98160000
30	861.33930000	8.34980000
31	910.44410000	38.57830000
32	945.83080000	41.45830000
33	961.55680000	5.45230000
34	971.25770000	23.34790000
35	988.80030000	9.64920000
36	1011.59130000	74.69380000
37	1047.69830000	4.06390000
38	1084.29180000	0.09160000
39	1097.10390000	41.29110000
40	1137.61930000	12.21710000
41	1138.90400000	128.13050000
42	1151.34460000	36.98740000
43	1163.78710000	189.37990000
44	1208.81230000	9.25590000
45	1253.84870000	12.59410000
46	1256.54450000	22.75230000
47	1275.24750000	1.57830000
48	1292.58420000	4.56590000

49	1298.21250000	3.73630000
50	1310.13190000	3.91760000
51	1342.22230000	8.74760000
52	1359.38090000	70.89270000
53	1387.85690000	24.92210000
54	1432.97070000	39.61920000
55	1450.52740000	8.87090000
56	1454.85850000	1.36450000
57	1460.42520000	52.62920000
58	1470.67880000	13.47560000
59	1481.27730000	3.10920000
60	1490.40790000	17.40260000
61	1495.12380000	14.28030000
62	1500.43190000	8.34370000
63	1509.93790000	32.61000000
64	1518.27410000	28.90660000
65	1521.38210000	28.66680000
66	1530.11180000	80.84350000
67	1602.32510000	11.00240000
68	1792.12630000	470.35760000
69	3046.72320000	10.54550000
70	3087.84290000	2.37770000
71	3094.83200000	9.33430000
72	3098.14520000	10.11360000
73	3112.67600000	7.76190000
74	3126.27200000	2.71380000
75	3173.07200000	0.75800000
76	3181.64980000	5.03800000
77	3183.50460000	4.45870000
78	3202.81100000	0.47370000
79	3205.96720000	3.53840000
80	3206.93720000	1.93850000
81	3254.62270000	0.78050000
82	3275.02350000	1.06730000
83	3641.80910000	154.59500000
84	3713.06540000	171.95110000

S26. HERCYNINE (CONFORMER C) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O	
Formula	: $C_9H_{16}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -667.45576054	a.u.
Gibbs Energy	: -667.23628500	a.u.
Number of imaginary frequencies	: 0	

S26.1. Cartesian Co-ordinates (XYZ format)

30

C	2.75465393	-1.28881204	-0.44597399
C	1.73173499	-0.38568500	-0.39089400
C	3.43010306	0.54733503	0.58123302
N	3.82115889	-0.67593098	0.17054600
H	2.81758595	-2.28011608	-0.85377097
N	2.16897798	0.75172901	0.25552201
C	0.33007801	-0.48424199	-0.90060902
H	0.12253700	-1.52550995	-1.12149501
H	0.22578201	0.05494000	-1.84299505
C	-0.68127102	0.07990200	0.13064601
H	-0.25790501	-0.01638400	1.12777197
N	-1.97885501	-0.72579902	0.20127600
C	-0.91351998	1.58304906	-0.13253599
O	-1.96925199	2.04130602	-0.51021397
O	0.14227900	2.33551598	0.06825600
C	-1.66156900	-2.11682510	0.68287599
H	-1.04334402	-2.63132811	-0.04046400
H	-1.14943004	-2.04845095	1.63691700
H	-2.59908700	-2.64848709	0.79932499
C	-2.67654610	-0.81568903	-1.12862206

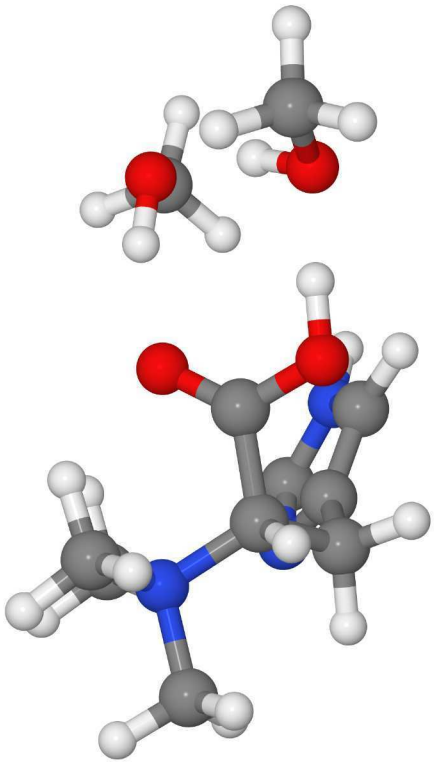
H	-2.91115499	0.18649399	-1.46047401
H	-2.02653790	-1.31647599	-1.83664894
H	-3.58125997	-1.39749897	-0.98791200
C	-2.91429496	-0.11895000	1.21859002
H	-3.75943494	-0.78935897	1.32911503
H	-2.38437700	-0.03133600	2.16172409
H	-3.23754501	0.84923500	0.86612397
H	1.00872397	1.80527604	0.26252401
H	4.73686695	-1.07454002	0.29898199
H	4.07369900	1.23566997	1.09876502

S26.2. Frequencies

Mode	IR frequency	IR intensity
1	45.96250000	2.06070000
2	72.73020000	1.15730000
3	90.86300000	1.76710000
4	113.75640000	4.27160000
5	161.49540000	10.00800000
6	202.66350000	9.38190000
7	228.65620000	14.24330000
8	244.33490000	7.67620000
9	257.69530000	8.82570000
10	262.15170000	14.40400000
11	280.56470000	5.79040000
12	322.05030000	14.62930000
13	332.76130000	17.40750000
14	364.70050000	6.29510000
15	376.50390000	7.15380000
16	429.41080000	1.90580000
17	438.77980000	1.43360000
18	487.38010000	4.35040000
19	555.97270000	7.75700000
20	598.67050000	140.27650000
21	657.56410000	4.42980000
22	674.89660000	28.49150000
23	683.56200000	8.38870000
24	730.28430000	1.53780000
25	764.03280000	16.04550000
26	794.21310000	16.74680000
27	816.47970000	28.36330000
28	851.84960000	9.44290000
29	856.78660000	38.24950000
30	913.96980000	51.83050000
31	946.02670000	34.76300000
32	967.47920000	11.01930000
33	975.39480000	22.53660000
34	1006.21710000	19.15150000
35	1021.26750000	17.42990000
36	1042.40380000	18.49600000
37	1067.71090000	159.28050000
38	1082.30350000	0.37100000
39	1097.42280000	63.68570000
40	1142.29890000	6.64670000
41	1153.44950000	4.76520000
42	1161.45540000	16.83830000
43	1215.56430000	26.84700000
44	1242.70550000	133.09880000
45	1248.28660000	28.80550000
46	1259.84000000	37.71640000
47	1275.44930000	52.85910000
48	1296.66010000	8.58180000

49	1303.44120000	11.62920000
50	1334.07780000	43.72710000
51	1354.61600000	13.74360000
52	1378.50800000	25.06480000
53	1425.55210000	8.94590000
54	1447.51490000	4.38280000
55	1451.45830000	21.54330000
56	1471.15760000	36.22280000
57	1474.77940000	3.17670000
58	1484.65930000	25.91750000
59	1489.81710000	5.47220000
60	1493.71920000	15.27470000
61	1504.08320000	13.86130000
62	1507.36940000	17.70590000
63	1521.86890000	53.76280000
64	1526.90550000	197.65940000
65	1532.10300000	127.36110000
66	1539.30690000	183.86520000
67	1616.69250000	97.79470000
68	1775.56810000	717.26450000
69	2450.67120000	3301.42540000
70	3054.24300000	13.13490000
71	3091.69380000	6.75480000
72	3094.32080000	5.44800000
73	3097.99190000	10.54860000
74	3100.38200000	1.54570000
75	3140.37990000	4.88060000
76	3174.27550000	2.21390000
77	3180.02960000	3.35840000
78	3181.26490000	6.07380000
79	3200.72950000	4.76140000
80	3209.31040000	1.93750000
81	3219.77310000	4.59200000
82	3272.36520000	3.39170000
83	3284.54910000	2.64010000
84	3636.49210000	175.12790000

S27. HERCYNINE (CONFORMER A) + 2 MEOH IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O.CO.CO	
Formula	: $C_{11}H_{24}N_3O_4^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -899.04546900	a.u.
Gibbs Energy	: -898.73476100	a.u.
Number of imaginary frequencies	: 0	

S27.1. Cartesian Co-ordinates (XYZ format)

42

C	0.05848500	2.13383603	-1.08497703
C	-1.15539205	1.51917803	-0.91522700
C	-1.24646401	3.36137104	0.19876800
N	-0.01518900	3.30134892	-0.36657101
H	0.70593500	3.99999690	-0.29554299
H	0.93500602	1.85673594	-1.64063001
N	-1.96245098	2.30239201	-0.11292900
C	-1.62441504	0.22455500	-1.49609005
H	-1.15251601	0.07996600	-2.46531892
H	-2.69265199	0.27458799	-1.68550503
C	-1.28802395	-1.07062995	-0.71360999

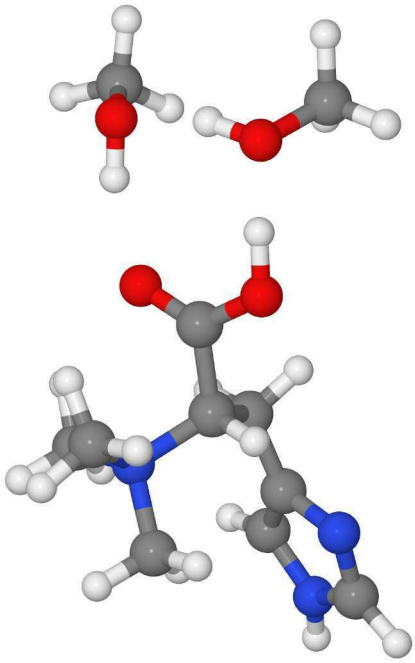
H	-1.40103805	-1.90283203	-1.40413105
N	-2.23150611	-1.42475200	0.43755201
C	0.18310700	-1.02613199	-0.30177701
O	0.57175702	-0.92590600	0.84886199
O	0.94113201	-1.07177603	-1.36294103
C	-3.62588692	-1.57785296	-0.10560600
H	-4.00497818	-0.61157900	-0.41165200
H	-3.60650396	-2.26564693	-0.94450700
H	-4.24839020	-1.97559500	0.68835002
C	-2.27098298	-0.40224800	1.54299903
H	-1.28020406	-0.31218699	1.96537197
H	-2.59711790	0.54651397	1.13301897
H	-2.97423410	-0.76155698	2.28701997
C	-1.82412505	-2.75871110	1.00758100
H	-2.55830097	-3.04119301	1.75397396
H	-1.81053901	-3.48837590	0.20410800
H	-0.84645998	-2.66482997	1.45999706
H	1.94713700	-0.95434499	-1.14583194
H	-1.56438601	4.18614197	0.81273103
O	3.41153598	-0.73114902	-0.90423799
H	2.14242291	-0.25685200	1.50931597
C	4.19966221	-1.92957306	-0.91423601
O	3.02771711	0.14229600	1.58102703
C	2.87325406	1.54277301	1.83158398
H	3.44049191	-0.33401799	0.00071700
H	3.86444592	1.98916698	1.80991006
H	4.10684204	-2.37509704	-1.90149105
H	5.24700880	-1.69432199	-0.72660899
H	3.84801006	-2.64046192	-0.16479699
H	2.25196695	2.01743388	1.07038605
H	2.42861009	1.71527505	2.81312895

S27.2. Frequencies

Mode	IR frequency	IR intensity
1	10.43340000	3.34400000
2	19.76640000	3.85860000
3	34.37480000	2.38300000
4	49.88840000	5.90800000
5	52.71020000	7.25870000
6	75.11950000	1.83130000
7	80.21780000	1.01790000
8	87.86920000	0.45190000
9	97.91210000	1.52000000
10	106.41900000	0.51210000
11	110.91220000	2.70320000
12	118.93160000	9.84950000
13	121.52090000	3.46150000
14	125.52280000	8.24710000
15	160.96550000	3.60330000
16	209.83650000	4.10760000
17	219.16990000	28.19520000
18	230.53300000	21.30150000
19	248.52580000	14.13850000
20	256.19280000	5.64920000
21	278.40690000	6.38090000
22	290.83020000	24.62870000
23	302.94780000	46.99890000
24	319.24770000	7.73740000
25	346.56040000	25.52810000
26	380.34300000	6.02850000
27	399.11600000	73.86840000
28	428.52300000	5.16590000
29	439.94610000	6.84660000
30	523.33390000	20.44740000
31	567.33280000	6.78080000
32	593.33730000	160.77920000
33	638.68190000	98.86230000
34	652.65620000	127.74740000
35	682.15050000	32.03120000
36	700.49630000	56.41000000
37	726.48780000	13.10780000
38	729.81610000	10.79620000
39	789.39080000	16.56100000
40	824.85840000	44.80220000
41	851.33090000	22.32670000
42	868.17610000	16.07300000
43	896.42580000	46.68850000
44	935.40940000	67.77110000
45	952.90080000	40.48360000
46	961.54740000	4.03770000
47	965.34190000	7.14440000
48	983.65830000	26.91090000
49	1012.29020000	36.68320000
50	1017.52120000	234.57640000
51	1030.66420000	22.17420000
52	1041.31730000	113.29890000
53	1083.92440000	0.58310000
54	1100.86580000	48.99910000
55	1115.81810000	28.67650000
56	1130.73470000	43.45890000
57	1145.15730000	14.91340000
58	1148.13710000	9.67180000
59	1149.25020000	2.41770000
60	1158.09200000	54.61900000

61	1180.85130000	1.46810000
62	1196.81400000	43.82100000
63	1213.35680000	72.74500000
64	1246.93620000	81.56880000
65	1249.53460000	35.50150000
66	1259.19030000	6.63350000
67	1287.28720000	38.47250000
68	1298.70150000	8.03570000
69	1313.34040000	179.87120000
70	1322.82150000	58.32080000
71	1366.58720000	14.55230000
72	1395.45430000	42.01700000
73	1414.71550000	26.71820000
74	1429.27370000	49.72210000
75	1445.66460000	0.91130000
76	1448.02390000	82.16000000
77	1456.02800000	19.66410000
78	1458.01120000	32.08600000
79	1467.98970000	34.23810000
80	1473.82290000	7.26820000
81	1477.90310000	4.61360000
82	1478.83510000	17.57880000
83	1489.99210000	5.53410000
84	1490.59470000	7.88880000
85	1490.91920000	16.41000000
86	1492.54020000	0.58420000
87	1497.47080000	4.99670000
88	1503.22080000	13.64750000
89	1506.68460000	10.96560000
90	1510.05190000	53.78330000
91	1520.65520000	53.43730000
92	1523.48360000	26.57760000
93	1533.63540000	78.83210000
94	1541.26660000	12.66110000
95	1591.15580000	8.98290000
96	1723.19100000	520.50840000
97	2462.05780000	3623.05880000
98	3021.62880000	136.10360000
99	3027.20020000	29.68560000
100	3080.04100000	52.80620000
101	3084.44210000	9.85170000
102	3086.32810000	23.90960000
103	3090.64950000	45.44060000
104	3091.32450000	8.66190000
105	3092.41660000	12.28190000
106	3105.86800000	10.00800000
107	3120.80220000	40.23240000
108	3125.65000000	51.21080000
109	3134.36330000	5.40870000
110	3169.60090000	3.21690000
111	3172.86590000	8.37580000
112	3177.60170000	6.88440000
113	3197.25650000	3.03480000
114	3206.35110000	2.83100000
115	3211.21660000	7.77240000
116	3255.72140000	0.72060000
117	3276.11440000	1.53710000
118	3290.62800000	1341.44490000
119	3591.12750000	868.12800000
120	3644.56830000	152.13740000

S28. HERCYNINE (CONFORMER B) + 2 MEOH IN MEOH



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular scrf=(solvent=methanol)	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O.CO.CO	
Formula	: $C_{11}H_{24}N_3O_4^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -899.04400660	a.u.
Gibbs Energy	: -898.73410100	a.u.
Number of imaginary frequencies	: 0	

S28.1. Cartesian Co-ordinates (XYZ format)

42

C	-3.06402707	-0.49913701	1.45354998
C	-2.25429201	0.11043500	0.53270698
C	-4.24564314	0.19860700	-0.27164301
N	-4.33098412	-0.43389699	0.92483902
H	-5.17041588	-0.78808200	1.35266495
H	-2.85962796	-0.95713198	2.40375209
N	-3.00421906	0.54364800	-0.54082501
C	-0.78121197	0.33065400	0.58551598
H	-0.35866901	-0.07596500	1.50112796
H	-0.58701301	1.40532100	0.61228800
C	0.00499100	-0.17215000	-0.63931400
H	-0.47019899	0.19815800	-1.54166996
N	0.05919000	-1.69538105	-0.81794202

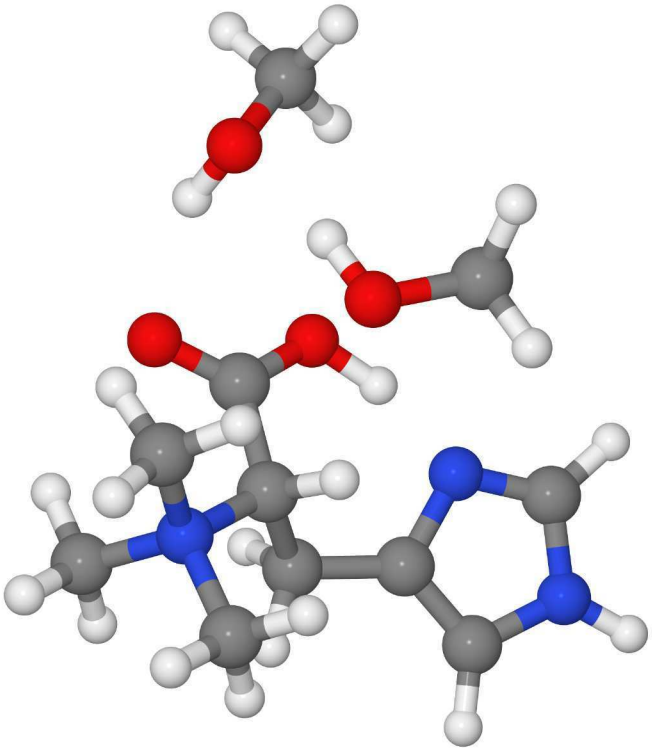
C	1.40163100	0.44026500	-0.53801000
O	2.28329611	-0.04830900	0.15064099
O	1.47682095	1.55411696	-1.20985198
C	-1.27084601	-2.19343710	-1.32172894
H	-2.02490711	-2.02391195	-0.56614500
H	-1.52271497	-1.66038704	-2.23160791
H	-1.16921401	-3.25470495	-1.52146900
C	0.39328301	-2.42621899	0.45236900
H	1.31371999	-2.02312398	0.85385001
H	-0.42415401	-2.30532694	1.15291703
H	0.50954598	-3.47656989	0.20694800
C	1.08590400	-2.03073192	-1.86841595
H	0.99269402	-3.08487010	-2.10464406
H	0.88430703	-1.43365896	-2.75227094
H	2.07434392	-1.82227802	-1.48054695
H	2.36998200	2.05951691	-1.06574595
H	-5.10499716	0.37945300	-0.89412099
O	3.61930609	2.87353802	-0.87828499
H	3.96462703	0.53276902	0.57509601
O	4.76460409	1.07065594	0.71733999
H	4.18792677	2.31504297	-0.29313901
C	3.37695003	4.13307285	-0.23571800
H	4.31478977	4.66687822	-0.08467800
H	2.73695397	4.71815014	-0.89131701
H	2.87782788	3.99862695	0.72535700
C	4.84701490	1.39758897	2.10833812
H	5.69078588	2.07160306	2.23546910
H	3.94017196	1.89576399	2.45750403
H	5.01611423	0.50250602	2.70924306

S28.2. Frequencies

Mode	IR frequency	IR intensity
1	8.59400000	3.52880000
2	18.44930000	2.69440000
3	24.36710000	0.66560000
4	48.93210000	0.96410000
5	58.92430000	1.88050000
6	72.47640000	4.10380000
7	74.16980000	3.70910000
8	78.00690000	1.08610000
9	88.11500000	9.07170000
10	109.49900000	0.99870000
11	114.36460000	1.64470000
12	119.71160000	1.68200000
13	125.24950000	2.37660000
14	149.26670000	2.30160000
15	163.84820000	19.51050000
16	198.19470000	8.32060000
17	218.80240000	35.91490000
18	231.74360000	10.52730000
19	249.94050000	12.29770000
20	271.11370000	3.33640000
21	276.91280000	19.14710000
22	282.94970000	17.95360000
23	293.19500000	35.04650000
24	327.19380000	19.62680000
25	357.03730000	33.30170000
26	369.50600000	4.80300000
27	389.82400000	78.78370000
28	423.26300000	9.98980000
29	439.37130000	20.64920000
30	485.90040000	10.56990000
31	579.12870000	8.64090000
32	580.59310000	157.62730000
33	655.17080000	91.72640000
34	659.04120000	102.43090000
35	675.65160000	9.25300000
36	710.36790000	28.13230000
37	723.62900000	27.36190000
38	758.10380000	12.61720000
39	792.43460000	30.24030000
40	812.53110000	9.19260000
41	852.61940000	51.64230000
42	859.65110000	3.86670000
43	913.67240000	102.60030000
44	926.88530000	115.05370000
45	948.06110000	78.04730000
46	961.49710000	3.53590000
47	974.84800000	24.47380000
48	989.54710000	16.47080000
49	1016.03420000	131.06210000
50	1019.52130000	29.83590000
51	1035.93880000	169.03800000
52	1049.76220000	1.17490000
53	1083.10160000	0.02880000
54	1097.99050000	47.59810000
55	1117.10140000	20.54850000
56	1133.43130000	48.63970000
57	1137.62640000	10.19400000
58	1143.82530000	11.40240000
59	1151.55510000	2.49220000
60	1158.22390000	63.50330000

61	1180.74410000	1.49610000
62	1194.29040000	39.90580000
63	1205.08120000	30.08670000
64	1245.37450000	60.87310000
65	1254.52910000	12.97480000
66	1274.02410000	16.07670000
67	1289.80720000	26.20940000
68	1296.96080000	3.97660000
69	1311.90780000	14.68120000
70	1335.23340000	300.92010000
71	1346.67430000	93.53120000
72	1389.39960000	32.06510000
73	1418.80860000	58.41990000
74	1425.52820000	55.72340000
75	1448.88750000	11.60290000
76	1450.84460000	0.24650000
77	1461.24850000	51.89550000
78	1467.54740000	54.01680000
79	1471.58650000	14.09990000
80	1475.15720000	1.29180000
81	1478.83460000	12.84200000
82	1480.35710000	5.80260000
83	1489.94200000	7.85040000
84	1491.08110000	19.07430000
85	1492.34140000	7.52660000
86	1493.21760000	20.81510000
87	1497.65380000	3.35960000
88	1504.88350000	11.30690000
89	1508.70680000	20.26730000
90	1510.17570000	13.77790000
91	1517.61310000	23.65020000
92	1521.68810000	27.22820000
93	1532.34860000	87.29610000
94	1564.04570000	34.18040000
95	1602.25400000	10.67110000
96	1715.33500000	574.36860000
97	2459.32140000	3767.56400000
98	3015.36440000	71.76190000
99	3026.80940000	65.17390000
100	3042.03690000	12.01920000
101	3072.19140000	66.02870000
102	3087.61010000	4.80880000
103	3090.65900000	46.80360000
104	3092.38350000	4.51640000
105	3095.95180000	13.53090000
106	3111.77940000	7.87650000
107	3118.73380000	42.77050000
108	3125.52610000	51.50110000
109	3135.17300000	1.93970000
110	3172.72950000	1.96790000
111	3178.23220000	2.66840000
112	3180.46540000	6.45630000
113	3199.94930000	0.53520000
114	3204.46010000	2.75570000
115	3207.85060000	2.34140000
116	3253.63170000	0.79040000
117	3273.42430000	1.09580000
118	3287.93540000	1262.96440000
119	3579.45830000	1045.54620000
120	3643.04650000	151.77350000

S29. HERCYNINE (CONFORMER C) + 2 MEOH IN MEOH (1st CONFORMER)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular scrf=(solvent=methanol)	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)O.CO.CO	
Formula	: $C_{11}H_{24}N_3O_4^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -899.04352356	a.u.
Gibbs Energy	: -898.73092800	a.u.
Number of imaginary frequencies	: 0	

S29.1. Cartesian Co-ordinates (XYZ format)

42

C	2.65594411	-1.41405499	0.38902301
C	1.75132596	-0.69747800	-0.34055799
C	3.53173995	0.53253299	-0.18634699
N	3.77695608	-0.61903399	0.47002101
H	2.60500193	-2.38508296	0.84446698
N	2.31281495	0.51367402	-0.68826199
C	0.35373300	-1.02697301	-0.75320899
H	0.04034800	-1.91400301	-0.21490499
H	0.31776199	-1.28372598	-1.81259596
C	-0.59817499	0.16611400	-0.47662801
H	-0.19117101	0.77988899	0.32262099

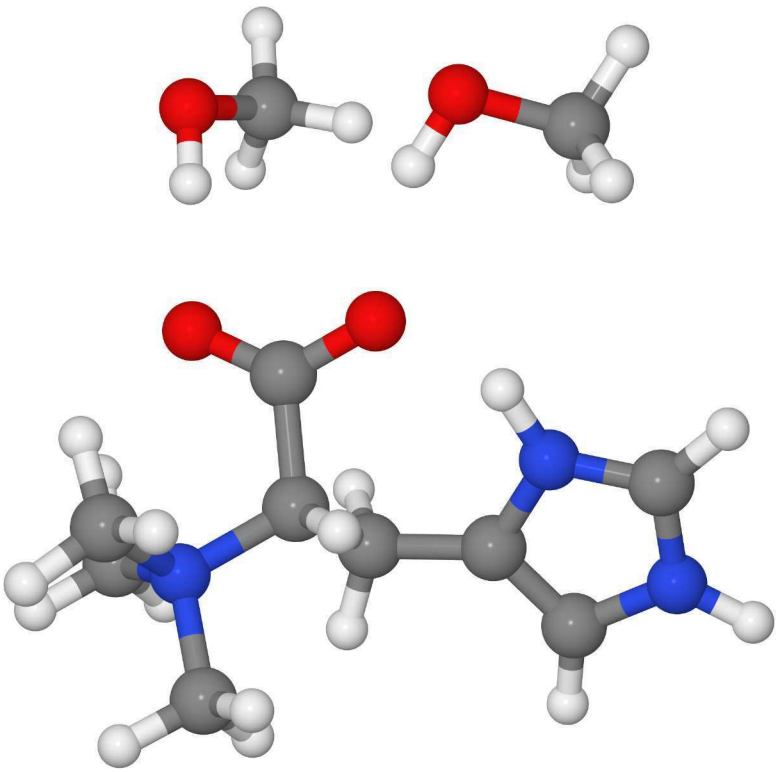
N	-1.96604097	-0.26378199	0.05301800
C	-0.67715901	1.08352101	-1.70880103
O	-1.71063006	1.31738603	-2.30966902
O	0.46112201	1.60439396	-2.08043694
C	-1.77104294	-0.94363201	1.38244200
H	-1.18804002	-1.84684598	1.26310003
H	-1.26811397	-0.25475800	2.05307198
H	-2.75087094	-1.19633198	1.77125001
C	-2.67555499	-1.20034206	-0.88273799
H	-2.81577802	-0.69703001	-1.83032703
H	-2.08413100	-2.10009789	-1.00693905
H	-3.63281202	-1.44976997	-0.43728301
C	-2.84323812	0.94031900	0.31675401
H	-3.70247793	0.59578800	0.88106000
H	-2.26819801	1.66524506	0.88263500
H	-3.15146303	1.36157596	-0.62791699
H	1.28497601	1.29860306	-1.51884794
H	4.63359022	-0.85262400	0.94511902
H	4.24318123	1.33405495	-0.27086800
H	-1.76500106	3.25459909	-2.40187502
O	-1.64808297	4.14561415	-2.03608298
O	-0.65854001	3.28680897	0.41672301
C	0.65850598	3.78560305	0.61499798
C	-0.68491000	4.83974314	-2.83435297
H	1.06795704	3.29847097	1.49864995
H	1.30872297	3.56037402	-0.23450500
H	0.66226703	4.86635590	0.78175902
H	-1.06220901	5.01188278	-3.84425592
H	-0.50433397	5.80121088	-2.35889912
H	0.25444600	4.28743982	-2.89148498
H	-1.01920104	3.68347001	-0.40092301

S29.2. Frequencies

Mode	IR frequency	IR intensity
1	25.52170000	6.30750000
2	31.77140000	2.13740000
3	49.42060000	5.61160000
4	61.10580000	0.30060000
5	63.73620000	2.49920000
6	78.33790000	1.10920000
7	81.13150000	8.00060000
8	92.32370000	1.64020000
9	103.36670000	7.25600000
10	108.01950000	12.47890000
11	112.88050000	3.18250000
12	121.09910000	0.58830000
13	131.88910000	2.94230000
14	155.66730000	8.52900000
15	171.75360000	18.35190000
16	175.00890000	7.11470000
17	213.00420000	30.84730000
18	219.63150000	9.48270000
19	236.93300000	10.46860000
20	248.14770000	9.64570000
21	260.77760000	0.84870000
22	263.21410000	32.85630000
23	296.31190000	11.91940000
24	324.30770000	8.64560000
25	341.63530000	21.03380000
26	369.36250000	10.32800000
27	379.79680000	12.88620000
28	433.33490000	3.23320000
29	442.43250000	1.91110000
30	486.37510000	14.89470000
31	558.39040000	6.19110000
32	596.85630000	190.41630000
33	598.77880000	178.49510000
34	653.84440000	3.79040000
35	670.07910000	31.03640000
36	684.84260000	15.73980000
37	729.94480000	5.06640000
38	754.12670000	43.31700000
39	789.69700000	77.65620000
40	810.17050000	96.48110000
41	821.93620000	170.68030000
42	856.17410000	8.34110000
43	857.49540000	49.97170000
44	914.90460000	44.60500000
45	941.10300000	29.47890000
46	969.98390000	7.84290000
47	979.89060000	17.33870000
48	1011.25660000	31.60870000
49	1024.96420000	28.84330000
50	1028.73230000	93.02980000
51	1045.76080000	1.70590000
52	1048.45520000	168.75580000
53	1084.02370000	0.55320000
54	1097.27000000	34.70200000
55	1106.62710000	17.75690000
56	1112.41630000	196.08270000
57	1136.06890000	15.92760000
58	1144.36630000	5.38250000
59	1153.36880000	9.75700000
60	1163.22660000	17.97510000

61	1176.32850000	2.24730000
62	1178.84070000	0.89150000
63	1212.49580000	32.97500000
64	1246.62390000	3.95580000
65	1250.55760000	99.81650000
66	1260.94910000	27.93320000
67	1279.49050000	60.73220000
68	1299.28090000	14.74750000
69	1303.11520000	24.03740000
70	1342.69640000	48.18680000
71	1353.69860000	36.49920000
72	1376.94540000	23.57390000
73	1404.20300000	50.28580000
74	1433.11000000	9.50930000
75	1449.98110000	18.35580000
76	1452.30870000	5.32730000
77	1465.18340000	27.86340000
78	1473.87090000	11.31200000
79	1474.09610000	22.81710000
80	1474.78890000	15.01920000
81	1479.04130000	0.87720000
82	1487.97650000	25.52190000
83	1488.27880000	13.92700000
84	1488.94480000	4.54140000
85	1489.17560000	12.38040000
86	1494.12510000	13.89790000
87	1505.84080000	20.33510000
88	1507.42790000	1.01320000
89	1508.92200000	13.36350000
90	1514.09140000	35.17840000
91	1521.02510000	46.33330000
92	1527.41840000	276.18350000
93	1539.09400000	106.98200000
94	1549.18650000	167.43620000
95	1619.88470000	120.41760000
96	1749.49860000	728.33600000
97	2313.01050000	3497.47730000
98	2998.18370000	84.30500000
99	3017.48510000	83.74830000
100	3046.21180000	78.16830000
101	3058.27240000	13.22140000
102	3075.14730000	55.38050000
103	3090.20330000	6.98010000
104	3092.22110000	4.63970000
105	3095.60170000	54.92620000
106	3097.87820000	23.85620000
107	3113.94920000	0.51840000
108	3115.54810000	40.24550000
109	3143.69130000	6.79650000
110	3175.34380000	3.19910000
111	3177.64410000	2.86960000
112	3183.32270000	2.79410000
113	3201.01870000	5.70670000
114	3202.93910000	1.04830000
115	3224.58820000	2.87450000
116	3274.43980000	4.04020000
117	3285.37440000	2.92060000
118	3487.44680000	818.32710000
119	3637.24400000	180.90150000
120	3654.83230000	530.30510000

S30. HERCYNINE (CONFORMER C) + 2 MEOH IN MEOH (2nd CONFORMER)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular scrf=(solvent=methanol)	
SMILES	: C[N](C)(C)C(Cc1c[nH]c[nH+]1)C(=O)[O].CO.CO	
Formula	: $C_{11}H_{24}N_3O_4^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -899.04260927	a.u.
Gibbs Energy	: -898.73007800	a.u.
Number of imaginary frequencies	: 1	

S30.1. Cartesian Co-ordinates (XYZ format)

42

C	2.80160904	-0.95396101	-0.26408800
C	1.70230997	-0.15868101	-0.37330499
C	3.35371804	1.07401204	0.44154301
N	3.81099892	-0.16065501	0.23943201
H	2.95014191	-1.99070895	-0.49710399
N	2.08146691	1.09082997	0.07277300
C	0.32634899	-0.44510701	-0.87250900
H	0.24176399	-1.52334404	-0.95969403
H	0.20944200	-0.04514400	-1.88019395
C	-0.77396601	0.14185899	0.04581900
H	-0.40672901	0.19580901	1.06688201

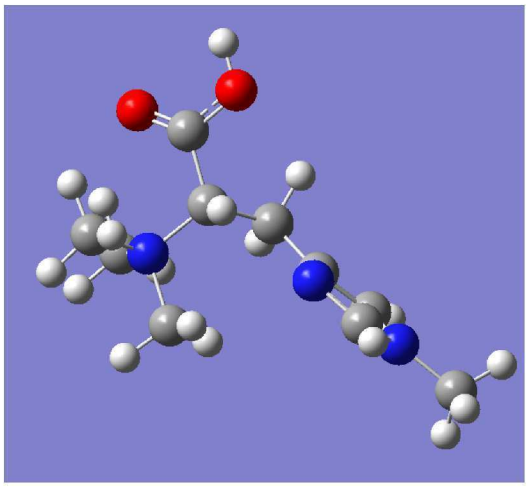
N	-1.99641705	-0.77558500	0.15204801
C	-1.09308505	1.59430003	-0.41574299
O	-2.14103007	1.82368004	-1.03676498
O	-0.18215799	2.41706800	-0.13093500
C	-1.60292006	-2.04284310	0.85928297
H	-0.87325501	-2.58681202	0.27361399
H	-1.19025302	-1.78764796	1.82959294
H	-2.49350095	-2.65013003	0.97887403
C	-2.58471489	-1.12285197	-1.18759501
H	-2.85188699	-0.20132700	-1.68681598
H	-1.85474396	-1.67963505	-1.76399004
H	-3.45860791	-1.74170697	-1.01357996
C	-3.04866409	-0.10593400	0.99877697
H	-3.84740090	-0.82062900	1.16425204
H	-2.59859800	0.17462800	1.94595397
H	-3.41329503	0.76499897	0.47322500
H	1.37911701	1.85708499	0.11617900
H	4.75329399	-0.46182799	0.43499801
H	3.91515493	1.90057397	0.83413702
H	-2.31737709	3.39308810	-1.87139499
H	0.00483100	4.21910715	-0.41916400
O	-2.40404296	4.18982506	-2.42916107
O	0.39934000	5.10689592	-0.48505899
C	1.80476904	4.94631100	-0.38738501
C	-1.35340202	4.15176105	-3.38197207
H	2.20162511	4.29492378	-1.17350399
H	2.26368499	5.92821789	-0.49836600
H	2.10732603	4.53909683	0.58403301
H	-1.39447296	3.25210810	-4.00610495
H	-1.45825696	5.01963186	-4.03337288
H	-0.37073299	4.20113993	-2.90406990

S30.2. Frequencies

Mode	IR frequency	IR intensity
1	-5.71230000	2.00300000
2	10.60240000	0.12350000
3	34.67440000	3.62840000
4	42.31820000	2.49130000
5	52.06460000	1.37790000
6	66.08130000	12.23180000
7	75.48230000	4.28880000
8	90.64120000	0.64940000
9	101.44690000	5.81390000
10	102.97410000	2.16850000
11	106.17040000	0.69150000
12	110.53990000	2.91810000
13	117.67430000	6.46220000
14	154.96180000	16.99210000
15	158.58980000	5.33690000
16	176.64360000	5.21810000
17	195.95750000	2.34670000
18	199.51550000	6.93330000
19	229.57890000	24.14260000
20	243.52750000	3.51410000
21	254.97200000	17.65930000
22	270.30490000	23.07360000
23	284.30450000	1.96720000
24	316.27560000	6.20690000
25	343.61330000	46.39270000
26	366.87210000	4.50130000
27	374.74120000	8.08610000
28	426.67880000	5.80240000
29	438.15480000	5.81810000
30	482.02750000	3.33070000
31	558.00640000	8.63480000
32	627.09010000	71.81720000
33	659.38550000	1.08780000
34	681.66260000	233.51920000
35	691.51800000	36.58210000
36	699.64510000	88.96330000
37	718.72430000	7.60340000
38	733.94660000	49.80700000
39	782.85330000	4.65420000
40	811.02780000	14.72660000
41	820.95020000	8.45910000
42	865.10940000	31.40770000
43	870.05760000	92.26500000
44	907.89560000	72.07440000
45	949.98200000	31.86040000
46	958.88900000	39.93570000
47	973.12380000	30.59700000
48	985.63640000	66.55810000
49	1008.48320000	26.28840000
50	1015.66880000	8.29610000
51	1050.95430000	11.16960000
52	1051.31680000	98.21760000
53	1052.70020000	157.73390000
54	1082.05710000	0.54400000
55	1098.17230000	21.42050000
56	1119.87690000	18.35450000
57	1128.47460000	22.65170000
58	1141.15640000	9.67450000
59	1152.72310000	3.00600000
60	1169.70950000	283.67900000

61	1178.02820000	2.72040000
62	1178.47280000	0.94100000
63	1195.50750000	7.89220000
64	1227.49050000	22.78650000
65	1248.93660000	5.43640000
66	1264.44370000	12.81660000
67	1289.47690000	33.82020000
68	1294.74200000	17.42410000
69	1306.20540000	21.19480000
70	1342.41710000	111.89140000
71	1368.57110000	18.21010000
72	1384.68830000	204.66680000
73	1425.66630000	57.07240000
74	1442.40460000	16.89450000
75	1447.96980000	83.80220000
76	1454.68080000	47.02620000
77	1458.28190000	181.13370000
78	1462.28590000	27.23340000
79	1472.77660000	2.56030000
80	1475.74640000	27.19020000
81	1476.83540000	0.02270000
82	1482.07220000	38.19310000
83	1486.45740000	3.18830000
84	1488.79570000	5.97940000
85	1489.98860000	3.13770000
86	1492.15140000	8.60110000
87	1502.28410000	9.08060000
88	1503.26690000	10.80900000
89	1507.66800000	18.15720000
90	1509.33550000	13.10030000
91	1518.08480000	42.84130000
92	1523.80260000	13.99020000
93	1533.40120000	80.28200000
94	1559.53710000	25.62480000
95	1653.52590000	690.53790000
96	1685.30130000	249.04450000
97	2976.32690000	95.72650000
98	2979.47700000	102.58290000
99	3015.69760000	91.92450000
100	3030.13210000	79.24350000
101	3057.23900000	1725.38810000
102	3062.81880000	6.84800000
103	3078.23500000	66.74600000
104	3085.83060000	70.92910000
105	3086.46710000	3.96270000
106	3090.53670000	8.08360000
107	3094.90150000	20.52150000
108	3106.80250000	4.80810000
109	3136.77330000	4.95550000
110	3170.19420000	1.46250000
111	3175.57460000	3.49510000
112	3177.84560000	9.84230000
113	3191.82210000	8.15760000
114	3205.74890000	4.54180000
115	3212.66950000	6.09930000
116	3297.62700000	25.28240000
117	3302.16830000	22.58480000
118	3509.09010000	1001.39810000
119	3574.40180000	1066.20070000
120	3626.78870000	239.37780000

S31. METHYL-HERCYNINE (CONFORMER A)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)O)[N](C)(C)C	
Formula	: $C_{10}H_{18}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -706.70265194	a.u.
Gibbs Energy	: -706.45739500	a.u.
Number of imaginary frequencies	: 1	

S31.1. Cartesian Co-ordinates (XYZ format)

33

C	2.52880812	0.29206800	-0.99441600
C	1.33861804	0.37779200	-0.32054400
C	2.84799409	0.01380100	1.16057301
N	3.48787999	0.06238500	-0.03338400
H	2.78060293	0.38974699	-2.03525400
N	1.55021501	0.19799399	1.02386606
C	-0.02953400	0.69675702	-0.85093099
H	-0.19207101	0.25112000	-1.83158600
H	-0.10943100	1.77328897	-1.00044894
C	-1.14807105	0.31248301	0.13513701
H	-0.71116602	0.37193099	1.13233101
N	-1.64331198	-1.13365197	0.00752300
C	-2.29809403	1.31282902	0.07555100
O	-3.41955900	1.10121500	-0.30523500
O	-1.86778402	2.49536204	0.52251297
C	-0.47937000	-2.07477999	0.17167000
H	0.20668800	-1.94512999	-0.65665698
H	0.03094200	-1.84579206	1.10033703
H	-0.87260097	-3.08650589	0.17737199
C	-2.30323505	-1.42777002	-1.31381404
H	-3.15857410	-0.77677298	-1.43422306
H	-1.58478296	-1.27315903	-2.11056399

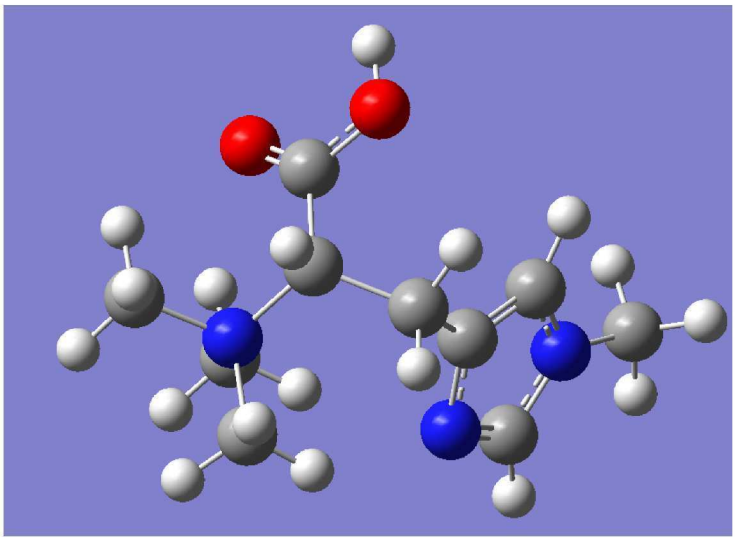
H	-2.60942698	-2.46943998	-1.30218101
C	-2.61689496	-1.42392194	1.12116599
H	-2.88068199	-2.47569108	1.07266700
H	-2.12883806	-1.20891404	2.06725001
H	-3.49923706	-0.81061298	0.99263197
H	-2.59739304	3.13293290	0.46543899
H	3.36745095	-0.15910400	2.08791900
C	4.91820908	-0.08236900	-0.26099500
H	5.32814693	0.83183402	-0.68606597
H	5.40607119	-0.27912501	0.68944502
H	5.11180115	-0.91327399	-0.93666703

S31.2. Frequencies

Mode	IR frequency	IR intensity
1	-6.70610000	0.69470000
2	38.51010000	1.92790000
3	64.26780000	2.49820000
4	81.29470000	1.52900000
5	93.13830000	2.61430000
6	125.15760000	3.78670000
7	164.68890000	8.15800000
8	193.61460000	2.30720000
9	215.92370000	0.23830000
10	251.51310000	1.69390000
11	268.57920000	2.02450000
12	275.01100000	0.96540000
13	290.90790000	3.91130000
14	300.39890000	0.76630000
15	316.07820000	0.54170000
16	339.79380000	1.13870000
17	364.55220000	10.73360000
18	384.88160000	2.56780000
19	429.29130000	1.50450000
20	438.83280000	0.45990000
21	495.70560000	2.48270000
22	549.42750000	9.37290000
23	603.89880000	77.75980000
24	632.19020000	10.22690000
25	642.63950000	28.35050000
26	669.74360000	39.39680000
27	682.22730000	7.24700000
28	730.33260000	21.01440000
29	751.71340000	8.74860000
30	773.83290000	6.93640000
31	795.65860000	19.64850000
32	845.35070000	24.07810000
33	865.16950000	17.18940000
34	910.41380000	23.77200000
35	949.01620000	25.95050000
36	969.04710000	14.21600000
37	1001.69870000	17.86370000
38	1011.38730000	37.69560000
39	1063.16110000	4.12970000
40	1072.68520000	2.90400000
41	1080.28920000	0.05840000
42	1085.15360000	9.19400000
43	1137.92930000	35.96730000
44	1151.36160000	1.90150000
45	1154.24370000	25.45480000
46	1171.50700000	155.67610000
47	1179.48670000	42.66920000

48	1221.25250000	1.52690000
49	1252.30700000	6.72540000
50	1257.94780000	34.73640000
51	1274.85350000	2.07160000
52	1289.30700000	6.75170000
53	1303.96840000	4.07830000
54	1321.16680000	14.97980000
55	1353.69800000	14.74950000
56	1362.85010000	62.09010000
57	1398.81330000	25.13030000
58	1417.81900000	1.09570000
59	1433.59630000	13.27130000
60	1445.78700000	14.16520000
61	1454.99840000	0.80980000
62	1459.88500000	24.02490000
63	1476.75630000	7.93990000
64	1480.56500000	2.90680000
65	1489.07830000	10.50150000
66	1491.52180000	34.19070000
67	1498.32230000	7.13790000
68	1502.26110000	0.81690000
69	1513.16980000	14.56130000
70	1517.88270000	14.06840000
71	1519.03460000	22.42160000
72	1534.05170000	81.02380000
73	1538.04550000	41.51980000
74	1588.71210000	3.62010000
75	1815.43500000	293.06620000
76	3055.89680000	25.75990000
77	3062.23500000	21.99340000
78	3071.23200000	17.59970000
79	3081.48150000	1.08420000
80	3085.03000000	2.87730000
81	3089.90810000	2.58970000
82	3095.11810000	10.53150000
83	3120.96700000	6.12470000
84	3146.76310000	3.16900000
85	3164.27590000	1.23590000
86	3170.57950000	1.24920000
87	3177.01980000	2.51840000
88	3188.06610000	2.06940000
89	3198.83870000	0.69990000
90	3207.53710000	6.15520000
91	3247.27010000	1.49050000
92	3260.17140000	1.22930000
93	3723.33290000	158.28690000

S32. METHYL-HERCYNINE (CONFORMER B)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)O)[N](C)(C)C	
Formula	: $C_{10}H_{18}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -706.70396666	a.u.
Gibbs Energy	: -706.45990700	a.u.
Number of imaginary frequencies	: 0	

S32.1. Cartesian Co-ordinates (XYZ format)

33

C	-2.17720294	0.67714798	-0.44005400
C	-1.13813698	-0.16418800	-0.74268901
C	-2.61271691	-1.35535502	0.26736501
N	-3.11354399	-0.09501400	0.20570999
H	-2.34036207	1.72041905	-0.64225900
N	-1.42424405	-1.43489802	-0.29336900
C	0.11372000	0.12237800	-1.49940801
H	-0.01832300	1.02397001	-2.09257698
H	0.29516301	-0.68010002	-2.21055794
C	1.40590894	0.37621799	-0.69332999
H	2.18684912	0.57292098	-1.42965698
N	1.95724297	-0.81452602	0.10750300
C	1.32195401	1.64835799	0.15424500
O	1.66805601	1.77250195	1.29769599
O	0.84526801	2.65126705	-0.59174699
C	1.88048196	-2.05790091	-0.73883301
H	0.83964700	-2.34610510	-0.84433901
H	2.33654308	-1.86210406	-1.70518601
H	2.43325400	-2.83770990	-0.22463600
C	1.22774994	-1.10620797	1.40179300

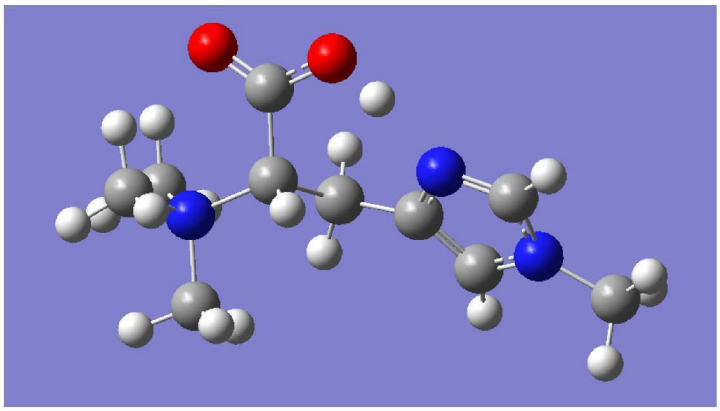
H	1.31182003	-0.24940699	2.05431700
H	0.19711301	-1.33929396	1.16564906
H	1.71287704	-1.97150099	1.84394002
C	3.40688992	-0.55091399	0.42263600
H	3.79515910	-1.40877998	0.96222299
H	3.95125389	-0.42584899	-0.50910997
H	3.47878003	0.33864099	1.03574002
H	0.85398501	3.45864892	-0.05308800
H	-3.15292311	-2.16810989	0.72306502
C	-4.41060495	0.35005099	0.69476402
H	-4.91015100	-0.48688799	1.17433798
H	-4.28609610	1.15055203	1.42132103
H	-5.02583694	0.70288801	-0.13074000

S32.2. Frequencies

Mode	IR frequency	IR intensity
1	27.28520000	3.90320000
2	36.61280000	3.66260000
3	53.58670000	1.10470000
4	73.33850000	0.21220000
5	102.47870000	0.58610000
6	133.42840000	3.78830000
7	172.47200000	5.91370000
8	206.25800000	4.62930000
9	226.59610000	0.28530000
10	235.52870000	3.36610000
11	270.36520000	0.93550000
12	283.20010000	1.27800000
13	313.96480000	4.84080000
14	340.71460000	2.10630000
15	343.09380000	3.32730000
16	365.05370000	4.27540000
17	378.18350000	1.95420000
18	417.38500000	1.21030000
19	435.83650000	1.65100000
20	445.16130000	1.67180000
21	521.25940000	12.34920000
22	545.03370000	8.76740000
23	600.51300000	1.70950000
24	606.62210000	36.07080000
25	646.88440000	21.60730000
26	661.73160000	62.74950000
27	689.30310000	41.10300000
28	717.60110000	7.57060000
29	743.25540000	5.21480000
30	783.69710000	14.20240000
31	807.05420000	21.06880000
32	852.47320000	20.93320000
33	865.64490000	2.91050000
34	888.39850000	44.63550000
35	951.55390000	19.20000000
36	961.09270000	10.58030000
37	985.02290000	15.24010000
38	1015.27580000	16.78250000
39	1042.38340000	36.95200000
40	1073.31700000	1.42210000
41	1084.39690000	6.17090000
42	1086.54070000	0.53550000
43	1145.79600000	28.63130000
44	1149.92130000	48.43660000
45	1151.64720000	0.70020000

46	1172.76200000	143.26100000
47	1184.89410000	40.02980000
48	1225.43290000	5.57390000
49	1249.80860000	2.05260000
50	1258.99930000	1.96010000
51	1270.51690000	11.42740000
52	1296.74530000	0.40170000
53	1302.96480000	5.75940000
54	1341.31160000	9.07720000
55	1345.85790000	18.47160000
56	1377.26120000	0.69000000
57	1391.52390000	11.06880000
58	1413.21130000	19.13390000
59	1427.65000000	0.59630000
60	1448.79300000	8.16840000
61	1451.94820000	4.82110000
62	1461.72890000	21.71020000
63	1481.98140000	14.00780000
64	1483.57490000	9.31570000
65	1489.54280000	11.04060000
66	1493.86260000	15.48320000
67	1501.77570000	12.77450000
68	1507.38210000	3.41860000
69	1516.75720000	18.11030000
70	1517.60310000	15.69080000
71	1526.67520000	2.53580000
72	1537.11590000	65.16730000
73	1545.44420000	34.04360000
74	1597.46840000	4.10680000
75	1821.25350000	240.78310000
76	3056.40880000	23.74070000
77	3059.49210000	1.76270000
78	3068.27510000	5.01840000
79	3080.52060000	2.30770000
80	3088.47530000	22.24040000
81	3090.59510000	22.05500000
82	3121.93000000	5.84270000
83	3125.66760000	1.09180000
84	3147.13040000	2.96820000
85	3159.58280000	0.47330000
86	3164.96840000	6.78840000
87	3167.93450000	1.19960000
88	3174.02010000	23.66950000
89	3194.52270000	1.76130000
90	3219.24010000	16.08860000
91	3245.92610000	1.38610000
92	3263.34710000	1.42050000
93	3722.21740000	140.59110000

S33. METHYL-HERCYNINE (CONFORMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)O)[N](C)(C)C	
Formula	: $C_{10}H_{18}N_3O_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -706.70716969	a.u.
Gibbs Energy	: -706.46270900	a.u.
Number of imaginary frequencies	: 0	

S33.1. Cartesian Co-ordinates (XYZ format)

33

C	2.50958109	-0.96101600	-0.57438600
C	1.38295698	-0.20344600	-0.40816200
C	2.98961401	0.84666502	0.58287901
N	3.52469110	-0.27707601	0.05866500
H	2.68318200	-1.89435804	-1.07858300
N	1.69893801	0.91901797	0.32120401
C	-0.01319100	-0.42410401	-0.90431899
H	-0.13418201	-1.48065901	-1.12683594
H	-0.17178400	0.10741300	-1.84484696
C	-1.05666804	0.05984400	0.13301501
H	-0.62358201	-0.00950600	1.12911403
N	-2.30160093	-0.83520800	0.20814800
C	-1.41995800	1.54352498	-0.13542201
O	-2.50761509	1.87493205	-0.54087502
O	-0.44743600	2.38633990	0.09459700
C	-1.89657605	-2.19802809	0.69327700
H	-1.23853004	-2.67190909	-0.02420700
H	-1.39496303	-2.09696198	1.65107095
H	-2.79457402	-2.79687691	0.80736399
C	-2.99663305	-0.97321600	-1.12110102
H	-3.29734993	0.01277000	-1.45120597
H	-2.31474209	-1.42900598	-1.83085299
H	-3.85990691	-1.61662996	-0.97952902
C	-3.27488399	-0.28128299	1.22309995
H	-4.07580996	-1.00389099	1.34407401

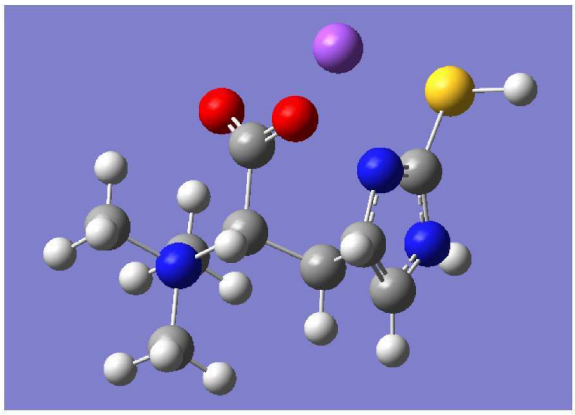
H	-2.74959207	-0.15026499	2.16510797
H	-3.65793109	0.66314399	0.86284399
H	0.43976599	1.93690896	0.31845999
H	3.56395292	1.56950104	1.13597298
C	4.91950512	-0.69239098	0.14072201
H	5.34668493	-0.76819801	-0.85695398
H	5.47342491	0.04975700	0.70805699
H	4.99600697	-1.65409100	0.64369798

S33.2. Frequencies

Mode	IR frequency	IR intensity
1	33.69270000	1.43630000
2	66.97690000	0.52300000
3	79.94640000	0.28820000
4	84.04670000	0.48950000
5	108.11220000	2.21860000
6	144.74270000	2.86130000
7	178.76750000	5.09910000
8	201.82480000	1.35150000
9	231.79870000	5.60240000
10	253.08850000	4.53110000
11	260.31730000	3.56590000
12	264.58900000	7.22060000
13	275.97240000	0.68620000
14	308.71320000	6.87360000
15	330.89480000	9.24890000
16	337.64450000	2.45300000
17	365.67010000	6.00710000
18	398.43940000	0.25590000
19	433.51670000	1.81170000
20	441.37780000	1.02360000
21	489.78810000	0.95990000
22	550.50040000	1.96720000
23	632.12000000	10.73360000
24	644.97000000	14.71280000
25	674.67990000	11.53210000
26	692.23930000	3.86870000
27	749.12640000	2.55230000
28	772.23930000	6.79850000
29	784.68930000	14.34330000
30	814.22740000	25.39570000
31	846.15120000	3.65350000
32	853.05430000	30.78200000
33	907.22810000	46.82220000
34	944.89500000	18.93530000
35	971.37590000	17.92600000
36	1002.41930000	5.17270000
37	1026.35230000	13.90210000
38	1036.12060000	53.47040000
39	1052.96760000	64.78800000
40	1073.47120000	9.89790000
41	1075.78080000	1.99830000
42	1090.84060000	10.78220000
43	1138.78100000	3.49280000
44	1149.83960000	3.25480000
45	1153.04230000	0.05120000
46	1182.46010000	28.62450000
47	1216.23180000	13.14980000
48	1241.45900000	18.82190000
49	1247.71540000	34.40980000
50	1262.48590000	36.72560000

51	1278.96980000	31.07870000
52	1295.21420000	6.48730000
53	1322.60510000	19.25670000
54	1340.45410000	18.60440000
55	1348.70450000	7.48610000
56	1387.92110000	6.16240000
57	1415.60700000	6.52380000
58	1424.72520000	2.09640000
59	1439.11410000	9.07200000
60	1447.40020000	18.18420000
61	1462.86120000	28.28640000
62	1475.72630000	0.95010000
63	1484.05620000	30.54420000
64	1489.20590000	11.86620000
65	1491.98420000	2.23780000
66	1496.85650000	2.43790000
67	1507.99300000	8.45220000
68	1508.90350000	7.54060000
69	1517.52500000	17.01180000
70	1522.22550000	79.87520000
71	1525.58690000	137.63270000
72	1539.58050000	51.37400000
73	1547.74510000	125.85890000
74	1606.16540000	21.46070000
75	1811.29420000	413.85850000
76	2739.33070000	2033.72140000
77	3042.83490000	7.52750000
78	3060.09140000	16.20890000
79	3079.07420000	2.90350000
80	3082.78320000	1.73970000
81	3086.53900000	7.20860000
82	3090.79710000	3.27170000
83	3114.84040000	8.08080000
84	3128.00410000	4.16840000
85	3151.67600000	2.14420000
86	3160.13540000	0.74870000
87	3166.30070000	1.84860000
88	3169.53460000	4.49650000
89	3187.09460000	3.54780000
90	3198.94330000	4.80550000
91	3209.95570000	9.67650000
92	3258.39120000	4.80860000
93	3266.71280000	2.37140000

S34. ERGOTHIONINE (1Nε+NA)$_{SH}$ (THIOL; ISOMER A)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.40766370	a.u.
Gibbs Energy	: -1227.20483500	a.u.
Number of imaginary frequencies	: 0	

S34.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.10372996	-2.22076893	-0.59231400
C	-0.52875400	-0.99553901	-0.81848699
C	-2.48319101	-0.61935198	0.03911400
N	-2.33582306	-1.96729004	-0.04226600
H	-3.02069306	-2.64755797	0.24378800
H	-0.75993001	-3.22082305	-0.78712499
N	-1.40787601	-0.00903200	-0.41844901
S	-3.87553000	0.18800600	0.75950402
C	0.79099298	-0.70976901	-1.47017395
H	0.60309100	-0.16105600	-2.39323092
H	1.24830997	-1.65214205	-1.76634502
C	1.79945600	0.19151200	-0.72750199
H	2.58087111	0.45220000	-1.43741500
N	2.57154202	-0.48575199	0.42300299
C	1.07936704	1.50569797	-0.32951301
O	0.82183200	1.73082995	0.87705302
O	0.70966101	2.16823196	-1.31578696
C	3.37299609	-1.63141596	-0.11305000
H	2.70765901	-2.41140389	-0.46375501
H	3.99888301	-1.27876198	-0.92766500
H	3.99486399	-2.02102804	0.68749899
C	1.68186402	-0.99194402	1.52423406
H	1.08984101	-0.15753201	1.87898600
H	1.04581702	-1.77451801	1.12866998
H	2.31883407	-1.38981402	2.30935693

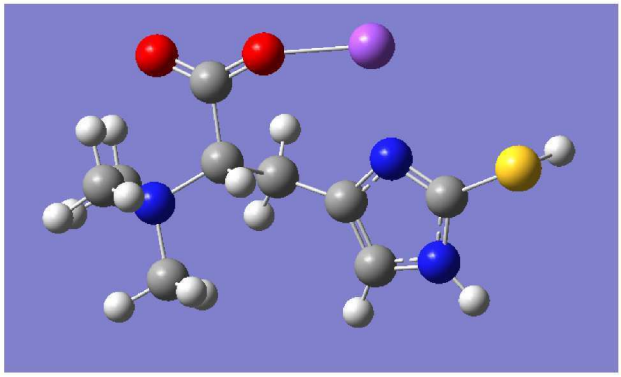
C	3.53367305	0.51996499	0.99968898
H	4.13637781	0.02079800	1.75266802
H	4.16952896	0.88774103	0.19931699
H	2.95935512	1.32816398	1.43485701
H	-4.63540888	0.22797000	-0.35471100
Na	-1.20945406	2.40784097	-0.07987700

S34.2. Frequencies

Mode	IR frequency	IR intensity
1	29.96520000	2.45270000
2	59.12040000	0.34330000
3	71.51740000	0.82100000
4	94.20420000	2.28910000
5	110.22140000	8.76060000
6	153.03130000	20.21450000
7	159.72690000	24.86030000
8	178.84470000	7.39960000
9	206.12300000	8.08080000
10	218.79960000	2.57780000
11	220.62020000	7.35790000
12	248.57930000	3.79600000
13	262.24880000	8.04810000
14	274.70350000	3.54200000
15	283.84230000	22.93760000
16	299.20760000	6.75470000
17	323.85620000	6.72280000
18	330.54870000	7.34910000
19	337.66690000	4.88140000
20	372.09950000	23.96510000
21	399.56280000	4.64480000
22	428.66620000	2.93640000
23	433.32950000	1.10870000
24	471.65530000	2.16970000
25	528.61370000	2.53350000
26	576.68590000	4.23620000
27	606.84130000	74.69520000
28	643.92830000	6.90860000
29	676.71230000	2.83840000
30	708.99340000	10.53760000
31	730.55450000	11.38910000
32	741.27790000	2.58210000
33	794.82660000	18.96340000
34	834.79100000	36.20340000
35	865.32830000	19.42330000
36	903.89480000	27.77150000
37	949.24990000	9.97600000
38	959.05100000	24.93830000
39	969.92340000	8.49010000
40	991.69650000	20.63640000
41	1002.58950000	2.00910000
42	1010.55900000	0.91370000
43	1049.57130000	3.74470000
44	1077.61390000	1.14180000
45	1117.93510000	33.43120000
46	1138.88100000	3.53370000
47	1148.20400000	3.17630000
48	1192.96240000	10.86280000
49	1229.73550000	11.49790000
50	1248.08520000	2.97870000
51	1262.14440000	13.63810000
52	1292.50650000	0.57340000

53	1297.50370000	4.39100000
54	1307.27030000	7.23810000
55	1347.24480000	5.75470000
56	1370.77670000	47.15660000
57	1400.11490000	14.28280000
58	1409.26130000	66.59850000
59	1434.33590000	2.87020000
60	1440.22280000	51.16770000
61	1446.97280000	14.13190000
62	1466.50660000	34.40350000
63	1478.15010000	9.93070000
64	1485.39250000	21.41570000
65	1489.69910000	20.34340000
66	1495.37930000	1.88630000
67	1505.95810000	4.79710000
68	1509.38550000	28.17860000
69	1523.23880000	20.81960000
70	1541.56180000	49.93270000
71	1591.27500000	22.65120000
72	1686.89680000	382.30100000
73	2635.08670000	1.20180000
74	3065.10480000	5.98810000
75	3073.90360000	4.45220000
76	3077.33370000	3.33540000
77	3082.63370000	21.67040000
78	3100.10750000	4.17930000
79	3102.40760000	11.49180000
80	3155.89550000	0.33390000
81	3161.34210000	5.34290000
82	3168.41200000	2.77260000
83	3178.74630000	5.78110000
84	3190.25310000	1.59140000
85	3194.62030000	9.98780000
86	3262.44040000	2.23640000
87	3638.03330000	122.04150000

S35. ERGOTHIONINE (1Nε+NA)$_{SH}$ (THIOL; ISOMER B)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.39811138	a.u.
Gibbs Energy	: -1227.19574500	a.u.
Number of imaginary frequencies	: 1	

S35.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.39690602	2.08431911	-0.52268302
C	-0.83031499	0.83858597	-0.61085403
C	-2.88945889	0.54832602	0.01059600
N	-2.69472909	1.88454497	-0.12145400
H	-1.00647700	3.06606388	-0.72104800
N	-1.77810204	-0.10667800	-0.27277300
S	-4.38640594	-0.18631600	0.58235902
C	0.56344098	0.48172101	-1.02219701
H	1.00577998	1.36924195	-1.46835995
H	0.52393103	-0.26088399	-1.81796396
C	1.45299101	-0.07220700	0.12314600
H	0.95137799	0.07232900	1.07667398
N	2.76981902	0.71883601	0.28841099
C	1.66990697	-1.61410105	-0.06946800
O	2.77247810	-2.02973795	-0.41463301
O	0.60419703	-2.24678206	0.13710400
C	2.46559310	2.13384891	0.66614801
H	1.92706800	2.62433290	-0.13608800
H	1.86563599	2.13654089	1.57143605
H	3.40224791	2.65510607	0.84142601
C	3.61399508	0.70478702	-0.95698202
H	3.79740095	-0.33175001	-1.21426404
H	3.08454108	1.21593404	-1.75364494
H	4.53861523	1.23207605	-0.74007499
C	3.56187010	0.10658800	1.41514003
H	4.43953800	0.72302699	1.58597004
H	2.93852997	0.09414500	2.30486298

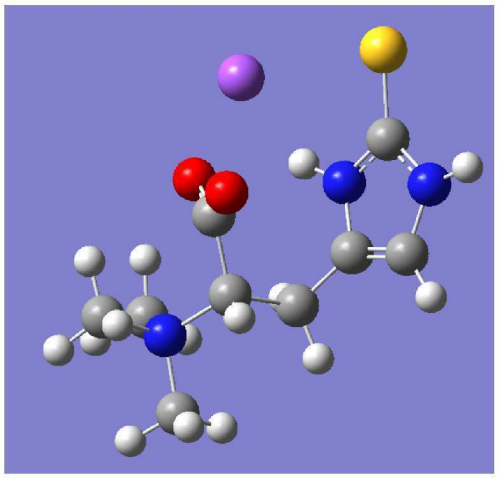
H	3.83819389	-0.89940900	1.12632501
H	-5.00603485	-0.24380100	-0.61475098
H	-3.39072990	2.59288812	0.04516400
Na	-1.49043798	-2.42619705	0.05853000

S35.2. Frequencies

Mode	IR frequency	IR intensity
1	-10.57160000	2.57800000
2	24.63160000	4.23050000
3	62.01280000	3.21710000
4	76.20790000	4.31590000
5	86.81140000	15.15930000
6	122.10270000	0.83070000
7	151.58630000	23.65490000
8	177.62280000	6.25760000
9	195.53950000	18.29120000
10	204.91820000	0.94030000
11	220.03180000	9.15870000
12	230.33330000	11.72370000
13	254.53780000	1.44400000
14	265.86640000	0.53070000
15	288.55750000	12.56240000
16	295.50890000	6.03150000
17	313.61480000	16.12130000
18	323.16480000	10.01850000
19	337.40480000	6.61630000
20	366.94630000	26.39020000
21	397.36200000	6.95050000
22	423.84700000	2.98640000
23	440.05620000	4.27460000
24	474.55420000	1.86800000
25	487.06250000	1.32410000
26	549.00620000	1.71220000
27	614.04810000	75.35520000
28	664.92070000	3.36880000
29	686.57110000	5.71680000
30	703.59770000	14.65280000
31	736.91580000	4.88370000
32	769.06370000	6.68120000
33	801.71660000	17.24620000
34	822.63060000	37.43570000
35	855.47720000	37.96430000
36	893.09860000	37.04150000
37	949.51300000	8.64590000
38	950.91440000	32.66280000
39	973.31060000	12.51550000
40	985.73730000	1.90340000
41	1007.28310000	3.11650000
42	1025.82060000	4.13590000
43	1038.43760000	2.14470000
44	1076.13560000	0.58690000
45	1119.74240000	35.10560000
46	1135.72640000	2.81140000
47	1148.62910000	3.57560000
48	1194.02690000	5.04910000
49	1228.76070000	1.73140000
50	1250.05050000	4.18530000
51	1252.61240000	24.62480000
52	1284.79420000	3.85410000
53	1289.00930000	1.24210000
54	1307.19320000	6.00080000

55	1356.82910000	7.81270000
56	1364.64220000	47.21620000
57	1367.96610000	136.84900000
58	1404.57840000	11.05160000
59	1428.28720000	13.79240000
60	1438.79960000	52.96910000
61	1443.23660000	22.37700000
62	1471.64830000	13.99700000
63	1477.80840000	29.84890000
64	1488.60470000	25.88680000
65	1491.74850000	1.82280000
66	1495.40470000	4.01750000
67	1506.48270000	8.03610000
68	1509.32410000	16.77110000
69	1523.68530000	25.43390000
70	1541.44880000	48.77370000
71	1593.44960000	35.13610000
72	1751.82170000	527.77370000
73	2635.63050000	1.11570000
74	3068.90960000	2.10580000
75	3072.62610000	7.61150000
76	3075.99260000	7.04900000
77	3081.31110000	18.72190000
78	3097.76950000	6.19990000
79	3108.22540000	11.39880000
80	3154.42310000	0.48230000
81	3159.59260000	6.95030000
82	3163.57500000	7.27040000
83	3176.91470000	6.98660000
84	3183.88720000	7.82530000
85	3192.84130000	15.02780000
86	3265.94750000	1.86500000
87	3636.76800000	123.23150000

S36. ERGOTHIONINE (1+NA)$_S$ (THIONE; ISOMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.41884860	a.u.
Gibbs Energy	: -1227.21205500	a.u.
Number of imaginary frequencies	: 0	

S36.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.32043898	-2.25046992	-0.71785200
C	-0.53763402	-1.59963095	0.17370801
C	-2.60331392	-0.65720201	0.26021501
N	-2.58581209	-1.68605196	-0.63037503
H	-3.37993789	-1.91400504	-1.20439303
H	-1.09005797	-3.03668690	-1.41186500
N	-1.36503994	-0.68629700	0.81254703
S	-3.79205108	0.50870198	0.52988702
C	0.93596900	-1.53639495	0.38469601
H	1.39111805	-2.46651912	0.05176200
H	1.13400400	-1.43055201	1.45044303
C	1.52610397	-0.33240199	-0.39462700
H	1.59999895	-0.58858299	-1.44741297
N	2.97041512	0.00594200	0.01809400
C	0.59619403	0.91363299	-0.30150399
O	-0.02133300	1.19105101	-1.34484398
O	0.46815401	1.46961904	0.81997597
C	3.88081288	-1.11546898	-0.38186499
H	3.60064697	-2.01617789	0.15267900
H	3.79909492	-1.27247596	-1.45336103
H	4.89999199	-0.84304601	-0.12358800
C	3.12593198	0.26517400	1.49326301
H	2.36281800	0.97485501	1.79310799

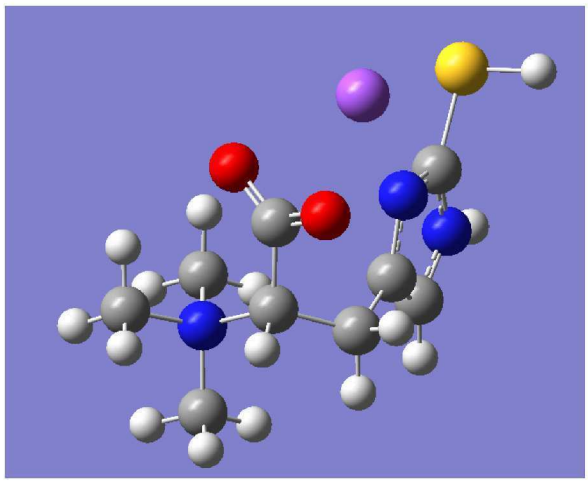
H	3.01863790	-0.66829199	2.03400612
H	4.12400913	0.66139197	1.65539503
C	3.38417411	1.24491000	-0.72894198
H	4.44292498	1.41298604	-0.55678201
H	3.19164801	1.09759402	-1.78718805
H	2.80653906	2.08371210	-0.35664701
H	-1.04000497	0.01647100	1.45857894
Na	-1.70451903	2.28275394	-0.18453000

S36.2. Frequencies

Mode	IR frequency	IR intensity
1	36.65330000	0.32040000
2	58.57380000	2.84590000
3	72.80050000	5.71880000
4	84.87200000	5.92890000
5	104.03220000	8.33860000
6	112.75060000	9.08020000
7	162.82800000	6.38590000
8	185.80580000	15.01110000
9	197.00540000	23.70760000
10	218.43660000	21.80660000
11	231.39630000	7.32960000
12	245.05640000	20.44370000
13	255.07890000	4.00710000
14	268.80020000	1.51790000
15	282.16710000	0.92150000
16	296.48480000	1.83160000
17	330.09470000	4.34970000
18	336.04770000	2.23290000
19	356.59370000	10.42730000
20	389.11570000	2.99630000
21	430.43020000	0.80320000
22	443.70230000	2.30100000
23	479.35540000	2.58810000
24	517.80640000	17.05410000
25	550.65430000	0.12490000
26	594.02990000	26.42340000
27	647.19540000	55.04190000
28	670.01490000	93.07730000
29	703.41930000	15.73030000
30	706.07110000	32.66960000
31	724.52860000	1.47710000
32	759.59820000	10.44790000
33	792.48890000	38.53600000
34	828.94460000	42.96950000
35	850.96890000	24.68780000
36	918.10670000	18.37940000
37	959.55290000	20.53530000
38	967.90470000	11.81380000
39	992.18690000	5.90210000
40	1001.45190000	3.19140000
41	1035.83220000	1.79740000
42	1041.80730000	2.95670000
43	1082.02080000	0.16490000
44	1102.13600000	33.24840000
45	1138.10190000	3.67980000
46	1151.08120000	0.57360000
47	1188.01430000	17.42220000
48	1198.67860000	50.16270000
49	1242.33330000	4.08170000
50	1266.34310000	10.87700000

51	1268.81470000	9.17560000
52	1289.62090000	7.71800000
53	1296.16840000	9.53630000
54	1327.37800000	5.39530000
55	1340.90350000	7.80230000
56	1382.52130000	58.74870000
57	1404.76990000	5.56260000
58	1410.46230000	61.34020000
59	1437.42940000	5.58290000
60	1445.49460000	18.36570000
61	1452.19310000	3.31350000
62	1481.83580000	0.52630000
63	1486.75780000	18.22390000
64	1488.52450000	24.32930000
65	1496.22490000	1.13490000
66	1500.89670000	6.23790000
67	1512.24330000	15.97060000
68	1517.92660000	123.94400000
69	1520.26540000	243.62340000
70	1535.63350000	36.01190000
71	1669.69230000	82.20800000
72	1683.99800000	279.31100000
73	3067.09510000	6.20830000
74	3075.63920000	1.61180000
75	3076.83600000	8.16400000
76	3082.49740000	15.71610000
77	3108.73640000	0.90970000
78	3123.60060000	4.40150000
79	3160.29130000	0.54280000
80	3165.08090000	2.15190000
81	3168.66360000	3.16950000
82	3176.39680000	2.03240000
83	3178.92340000	1.75370000
84	3182.59940000	11.07820000
85	3283.10400000	6.66300000
86	3597.31040000	123.30780000
87	3650.53920000	129.71480000

S37. ERGOTHIONINE (1Nε+NA)$_{SH}$ (THIOL; ISOMER A) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.50087343	a.u.
Gibbs Energy	: -1227.30004600	a.u.
Number of imaginary frequencies	: 0	

S37.1. Cartesian Co-ordinates (XYZ format)

31

C	-1.00742197	-2.24096107	-0.64108598
C	-0.48812699	-0.98850000	-0.85103798
C	-2.41497803	-0.71090502	0.09270300
N	-2.22216702	-2.04829311	-0.03820800
H	-2.86905503	-2.76400805	0.25003299
H	-0.62283999	-3.22059798	-0.85916603
N	-1.38044298	-0.04345600	-0.38628000
S	-3.83676100	-0.01147400	0.86716300
C	0.80653101	-0.64166200	-1.51409602
H	0.59864902	-0.05950700	-2.41107202
H	1.28576601	-1.55686903	-1.85212898
C	1.80375600	0.24021301	-0.73926002
H	2.61649489	0.47023001	-1.42404306
N	2.51820588	-0.46049500	0.43017700
C	1.12804997	1.59122300	-0.37840700
O	0.93210500	1.90144897	0.81839597
O	0.76104403	2.23610497	-1.38499296
C	3.23195791	-1.68009305	-0.07340100
H	2.50950789	-2.43074799	-0.36744201
H	3.85563302	-1.40254998	-0.91721398
H	3.84720492	-2.06651306	0.73240399
C	1.59766603	-0.87559497	1.54478395
H	1.06909704	0.00385000	1.88591099

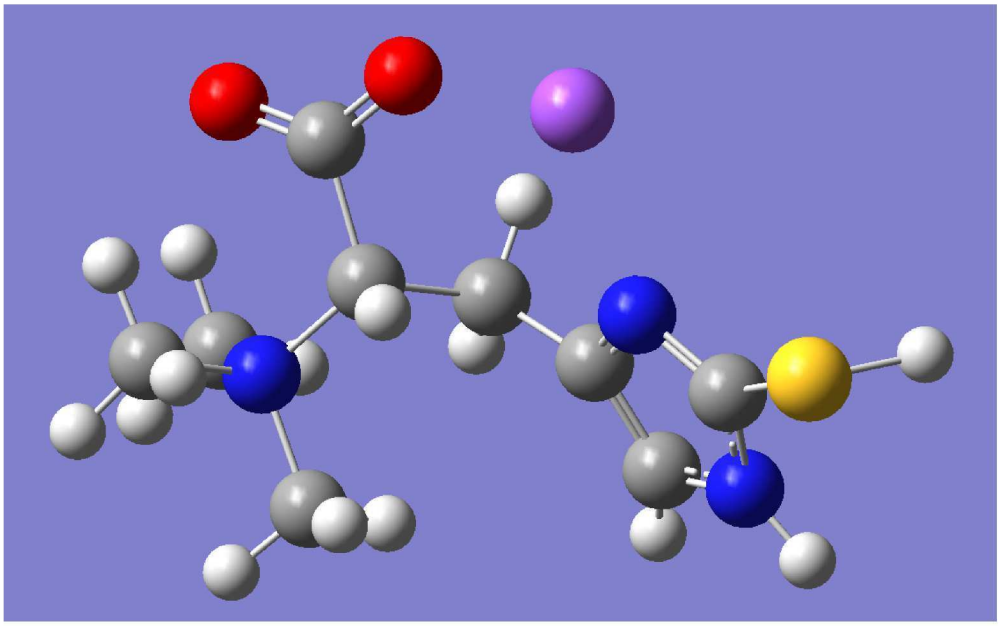
H	0.90708703	-1.61927903	1.16919804
H	2.20999098	-1.30082095	2.33381510
C	3.55752110	0.47758400	0.98136300
H	4.10426283	-0.04412300	1.75999296
H	4.23154879	0.75531298	0.17697600
H	3.05350995	1.34746099	1.38039696
H	-4.59479094	0.09139500	-0.24280800
Na	-1.28320098	2.45079803	-0.09616700

S37.2. Frequencies

Mode	IR frequency	IR intensity
1	21.69450000	5.81500000
2	48.40790000	13.56980000
3	66.97540000	10.54780000
4	82.58210000	23.74040000
5	91.68740000	21.23570000
6	104.90570000	2.04070000
7	128.59800000	5.65890000
8	146.07960000	49.30920000
9	174.16090000	13.38970000
10	191.31160000	4.78840000
11	212.85410000	36.24180000
12	217.46820000	9.66900000
13	251.76470000	19.92330000
14	266.00760000	2.58540000
15	276.69600000	3.73870000
16	304.57630000	10.26070000
17	325.26500000	7.16540000
18	331.44300000	11.94170000
19	346.26170000	4.56610000
20	363.55780000	24.09550000
21	407.85090000	8.41470000
22	424.25470000	3.37300000
23	437.69800000	1.31340000
24	469.85430000	2.63270000
25	533.35040000	3.79510000
26	581.69220000	8.15000000
27	608.84460000	127.01110000
28	644.96480000	13.75640000
29	676.41920000	6.55060000
30	698.22370000	16.12950000
31	731.50180000	18.40830000
32	737.66200000	3.79950000
33	799.96510000	26.50990000
34	833.85010000	59.13080000
35	868.56520000	23.80010000
36	900.50220000	49.17000000
37	942.87940000	24.92910000
38	958.64020000	46.25940000
39	970.04440000	5.83890000
40	999.80720000	30.57010000
41	1003.23720000	18.46710000
42	1010.62560000	1.20740000
43	1053.09140000	6.81430000
44	1081.11780000	1.28210000
45	1116.50060000	56.61600000
46	1145.41970000	6.07160000
47	1149.86710000	4.39090000
48	1198.88040000	21.41190000
49	1232.83840000	27.40760000
50	1246.34610000	3.15800000

51	1262.38170000	20.78840000
52	1294.33640000	2.28610000
53	1300.00120000	5.18880000
54	1309.77470000	20.56370000
55	1343.89170000	16.10790000
56	1368.96000000	107.71030000
57	1402.89380000	67.97080000
58	1412.54370000	48.27950000
59	1432.24850000	81.91870000
60	1436.85900000	42.38420000
61	1447.67090000	25.57820000
62	1466.06720000	51.36750000
63	1478.66190000	17.27730000
64	1485.07360000	17.77410000
65	1487.17150000	36.72510000
66	1491.85550000	5.06410000
67	1501.31680000	2.63010000
68	1506.27550000	43.20100000
69	1519.45980000	35.55310000
70	1534.66850000	78.50730000
71	1593.48270000	33.90470000
72	1642.86930000	739.34560000
73	2642.62490000	4.33060000
74	3072.00050000	9.56680000
75	3083.45710000	7.13190000
76	3084.02240000	11.72220000
77	3091.25340000	35.06110000
78	3100.61310000	11.53810000
79	3115.60700000	17.43620000
80	3166.42260000	1.51500000
81	3168.67670000	12.68420000
82	3178.00730000	1.54540000
83	3189.51590000	9.09930000
84	3201.06530000	2.80930000
85	3207.89260000	6.04680000
86	3268.82850000	2.12450000
87	3638.03650000	170.91870000

S38. ERGOTHIONINE $(1N\varepsilon{+}NA)_{SH}$ (THIOL; ISOMER B) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(n1)S)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.50098901	a.u.
Gibbs Energy	: -1227.30134300	a.u.
Number of imaginary frequencies	: 0	

S38.1. Cartesian Co-ordinates (XYZ format)

31

C	1.29685402	-2.07443905	-0.80730700
C	0.73420602	-0.83073503	-0.70649803
C	2.68069100	-0.70353502	0.23176000
N	2.52517390	-1.98049402	-0.19959500
H	0.94580603	-2.98965311	-1.24734998
N	1.61163795	0.01499800	-0.05765700
S	4.07823515	-0.12142300	1.13299894
C	-0.58977801	-0.33907500	-1.19061506
H	-1.09726596	-1.13970494	-1.72140896
H	-0.42593300	0.44802099	-1.92438602
C	-1.47689295	0.25007901	-0.06615200
H	-0.88954699	0.31046200	0.84600198
N	-2.63598299	-0.68038702	0.32666299
C	-1.88943696	1.71425605	-0.40763101
O	-3.07169509	1.99584496	-0.65413201
O	-0.89583999	2.48439002	-0.40741500
C	-2.07977891	-1.99992895	0.77214700

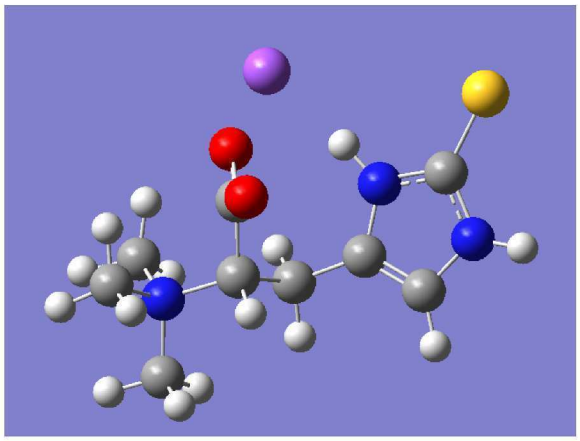
H	-1.59680498	-2.49341989	-0.06152400
H	-1.36307704	-1.82700002	1.56834400
H	-2.90092206	-2.61083007	1.13247001
C	-3.61149096	-0.91095197	-0.79200000
H	-3.98457503	0.05404700	-1.10808802
H	-3.10972190	-1.41769600	-1.60776496
H	-4.40972185	-1.54051304	-0.41210201
C	-3.36763310	-0.07541200	1.49269402
H	-4.13144398	-0.77594298	1.81441796
H	-2.65521097	0.09024300	2.29474401
H	-3.80820894	0.85824299	1.16973305
H	4.97250509	-0.21922299	0.12954400
H	3.19315505	-2.72529197	-0.08596600
Na	1.28437304	2.42074895	0.16104300

S38.2. Frequencies

Mode	IR frequency	IR intensity
1	27.59450000	12.07090000
2	33.91490000	5.31130000
3	55.43510000	1.81050000
4	73.98130000	27.02590000
5	78.49650000	23.11510000
6	91.68280000	30.62850000
7	114.36120000	0.24560000
8	144.79240000	28.80470000
9	173.95690000	13.12560000
10	191.95790000	25.46900000
11	216.39320000	3.62170000
12	227.70200000	13.58090000
13	233.25610000	48.55870000
14	256.28590000	14.26270000
15	269.29990000	1.57380000
16	298.61830000	2.88640000
17	309.24100000	14.87670000
18	319.28850000	4.73440000
19	341.67890000	4.97780000
20	356.86820000	15.29340000
21	391.59510000	12.24130000
22	423.37390000	1.94700000
23	437.24530000	3.54110000
24	475.23380000	1.70130000
25	492.49800000	3.51730000
26	554.15570000	2.38250000
27	599.39890000	131.32650000
28	657.53040000	3.37760000
29	685.37200000	3.60500000
30	708.35710000	44.39080000
31	734.99640000	3.17930000
32	763.42900000	13.57500000
33	800.59390000	21.11740000
34	821.73470000	59.10030000
35	864.39640000	31.81980000
36	903.83540000	63.96570000
37	945.44010000	17.23240000
38	957.23280000	48.49070000
39	974.14650000	12.59330000
40	999.55610000	4.10390000
41	1007.84940000	14.97490000
42	1024.09050000	8.80190000
43	1048.00030000	2.21330000
44	1079.97760000	0.61280000

45	1111.53640000	58.10460000
46	1141.92900000	2.32200000
47	1152.92810000	6.44150000
48	1201.04600000	7.91270000
49	1235.55570000	4.67500000
50	1258.36240000	37.07840000
51	1270.03560000	16.78850000
52	1289.89580000	3.54590000
53	1291.53910000	2.19920000
54	1301.60930000	13.82300000
55	1352.12860000	9.85450000
56	1369.36370000	338.56660000
57	1380.28880000	15.67850000
58	1415.56190000	3.49170000
59	1432.83080000	45.08410000
60	1438.93850000	59.80640000
61	1446.98330000	34.40690000
62	1469.21710000	25.51020000
63	1480.97620000	7.58690000
64	1485.30110000	32.55550000
65	1488.59960000	48.76850000
66	1489.94550000	15.18480000
67	1497.19320000	5.60540000
68	1506.93810000	32.04090000
69	1517.66590000	43.89800000
70	1529.48350000	76.03690000
71	1602.67940000	45.78170000
72	1673.22650000	847.06380000
73	2649.66990000	2.62230000
74	3075.95610000	9.84700000
75	3081.31250000	11.58980000
76	3087.12020000	6.82230000
77	3091.06600000	24.92680000
78	3103.27570000	6.22680000
79	3123.07800000	15.31120000
80	3164.18210000	4.45800000
81	3171.29600000	9.67290000
82	3173.81980000	11.23330000
83	3191.36670000	6.70130000
84	3198.40890000	0.55940000
85	3201.76040000	12.30160000
86	3273.23360000	1.54640000
87	3638.98700000	171.56100000

S39. ERGOTHIONINE (1 + NA)$_S$ (THIONE; ISOMER C) IN MEOH



Route	: # opt freq b3lyp/cc-pvtz scrf=(solvent=methanol) geom=connectivity emp	
	: iricaldispersion=gd3bj int=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]c(=S)[nH]1)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2S^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -1227.52112127	a.u.
Gibbs Energy	: -1227.31647300	a.u.
Number of imaginary frequencies	: 0	

S39.1. Cartesian Co-ordinates (XYZ format)

31

C	1.27904904	2.37574601	-0.60722101
C	0.60981202	1.48357904	0.15835100
C	2.79802990	0.87881702	0.15336400
N	2.61184311	1.99581397	-0.59566301
H	3.36232495	2.46269298	-1.07527399
H	0.93054199	3.23469400	-1.14821696
N	1.56272900	0.58743501	0.62599099
S	4.23769093	0.02752500	0.42291999
C	-0.83459097	1.34372699	0.49470901
H	-1.31890094	2.30132604	0.32306901
H	-0.92278397	1.10331595	1.55216801
C	-1.49387395	0.24216400	-0.34983101
H	-1.52700305	0.54737502	-1.39093697
N	-2.96578908	0.00895100	0.02527900
C	-0.67880702	-1.07910097	-0.27360699
O	-0.30462000	-1.56222999	-1.36070597
O	-0.40480101	-1.51814306	0.87395900
C	-3.77771497	1.21317196	-0.35512400
H	-3.44972992	2.06852102	0.22244699
H	-3.64899397	1.39991200	-1.41608202
H	-4.81923580	1.00321996	-0.13529800
C	-3.16086292	-0.27429301	1.48882306
H	-2.47245908	-1.05797303	1.78074598
H	-2.97231507	0.62894601	2.05631089

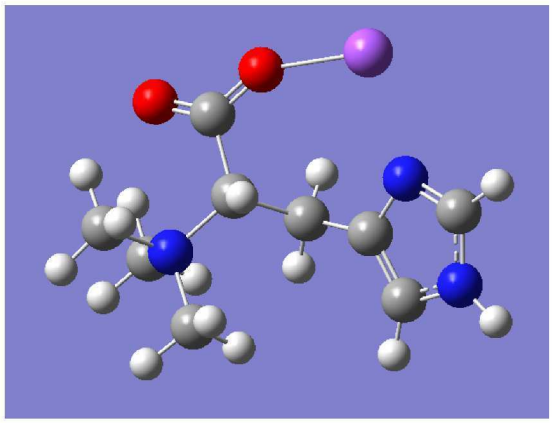
H	-4.19108486	-0.58295101	1.63066602
C	-3.47714305	-1.16538298	-0.76137799
H	-4.54507923	-1.24834895	-0.59043199
H	-3.27325702	-0.99737900	-1.81313896
H	-2.97461605	-2.06320000	-0.42071500
H	1.34111202	-0.23239800	1.17145705
Na	1.21035302	-3.03399491	-0.20583300

S39.2. Frequencies

Mode	IR frequency	IR intensity
1	26.62140000	3.79500000
2	44.78510000	4.86690000
3	49.98320000	2.73510000
4	64.25060000	25.30930000
5	72.64190000	2.94770000
6	99.15040000	53.55780000
7	115.26040000	9.33700000
8	154.30230000	17.78820000
9	185.25980000	42.70080000
10	201.21030000	1.58070000
11	214.80500000	45.62740000
12	221.48190000	3.62310000
13	253.45720000	5.32790000
14	268.84850000	3.35130000
15	284.22860000	2.40970000
16	298.61040000	3.04750000
17	326.52210000	0.73210000
18	335.75350000	19.69870000
19	353.56940000	4.72420000
20	392.25450000	4.76400000
21	433.12750000	2.35760000
22	444.95340000	2.37650000
23	485.18590000	12.55180000
24	512.91780000	45.07970000
25	554.26500000	2.45730000
26	583.33310000	89.65570000
27	653.76230000	2.78530000
28	685.85470000	24.56770000
29	687.42170000	22.56730000
30	722.13870000	16.11820000
31	739.86050000	143.76410000
32	764.17010000	15.98560000
33	801.28480000	84.86120000
34	833.02400000	55.87280000
35	860.59580000	33.57620000
36	918.76250000	23.16240000
37	961.51920000	33.29530000
38	973.87680000	17.06140000
39	996.93790000	11.96950000
40	1000.19290000	18.34620000
41	1037.67600000	1.24840000
42	1065.95720000	5.51440000
43	1083.94360000	0.23270000
44	1101.20540000	58.78500000
45	1142.18740000	4.90510000
46	1159.20340000	1.28990000
47	1185.69220000	106.01520000
48	1204.05980000	15.20250000
49	1247.05530000	5.98490000
50	1265.82740000	1.17830000
51	1270.38090000	28.83300000

52	1292.00600000	24.29850000
53	1298.62330000	22.75770000
54	1337.27640000	45.85400000
55	1353.81540000	7.80840000
56	1389.35090000	112.09630000
57	1407.15700000	20.03800000
58	1417.33850000	125.13150000
59	1431.94490000	13.95010000
60	1453.93000000	17.11220000
61	1455.31280000	9.46750000
62	1479.07200000	23.16170000
63	1482.68940000	34.88630000
64	1486.21970000	12.43880000
65	1491.18150000	13.94800000
66	1499.77880000	8.91220000
67	1502.40890000	621.79550000
68	1507.09390000	30.92600000
69	1516.11630000	24.86310000
70	1529.09020000	64.21590000
71	1639.66930000	711.78510000
72	1673.65430000	111.93380000
73	3077.87130000	7.78360000
74	3087.31570000	9.22830000
75	3088.32690000	2.90650000
76	3093.09340000	20.59370000
77	3119.36810000	1.20030000
78	3134.05080000	9.89170000
79	3174.66290000	3.07460000
80	3177.37090000	3.10550000
81	3180.95530000	7.02270000
82	3184.91370000	2.90570000
83	3190.37390000	4.36080000
84	3193.80330000	5.02650000
85	3289.50020000	6.65430000
86	3588.63960000	286.59630000
87	3653.79140000	161.55210000

S40. HERCYNINE (2 + NA) (ISOMER A)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -829.16847604	a.u.
Gibbs Energy	: -828.96360300	a.u.
Number of imaginary frequencies	: 0	

S40.1. Cartesian Co-ordinates (XYZ format)

30

C	2.19399309	-1.82326996	-0.42103001
C	1.55676401	-0.61347598	-0.44338900
C	3.50715590	-0.27951699	0.44082600
N	3.42762399	-1.59387600	0.14411999
H	1.89801204	-2.79720807	-0.76511198
N	2.39738798	0.34816900	0.10165200
C	0.19401100	-0.29620600	-0.97401100
H	-0.14136299	-1.14945996	-1.55848300
H	0.26787901	0.53022403	-1.67862797
C	-0.85062802	0.08949500	0.10662000
H	-0.39216501	0.01970300	1.09037900
N	-2.02411294	-0.91026002	0.19107699
C	-1.30144596	1.58174503	-0.08093600
O	-2.46828508	1.83788502	-0.35924599
O	-0.32595000	2.36026907	0.07649900
C	-1.50554299	-2.27727890	0.50719398
H	-0.89788097	-2.64085698	-0.31266299
H	-0.91151297	-2.22898889	1.41503501
H	-2.35119510	-2.94335198	0.65200001
C	-2.82694697	-0.96339899	-1.08006096
H	-3.18777609	0.03821500	-1.28135002
H	-2.19518900	-1.31779695	-1.88733697
H	-3.64693189	-1.65976501	-0.92928803
C	-2.93321300	-0.49505299	1.31954396
H	-3.71701598	-1.24086797	1.41412604

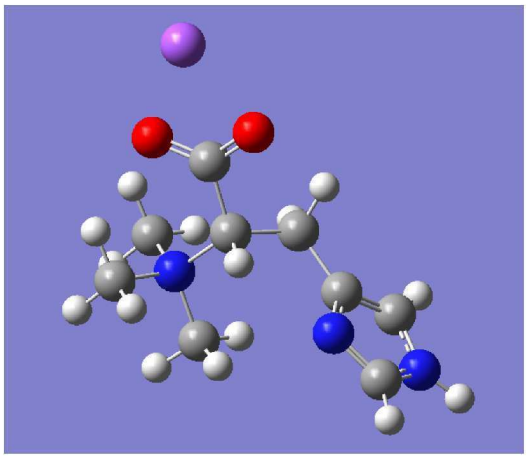
H	-2.34747100	-0.45534301	2.23369288
H	-3.34253097	0.47846699	1.08153701
H	4.14900112	-2.27935505	0.29482299
Na	1.75036800	2.62945604	0.24748400
H	4.37725782	0.16666700	0.89098001

S40.2. Frequencies

Mode	IR frequency	IR intensity
1	26.68220000	7.45470000
2	40.90870000	1.00680000
3	81.05690000	2.40510000
4	95.82360000	25.98890000
5	107.08480000	3.14880000
6	134.42140000	2.98330000
7	187.70340000	9.48550000
8	208.82230000	15.13120000
9	223.60580000	4.89040000
10	243.43270000	7.46690000
11	249.32370000	4.31570000
12	267.89160000	0.55110000
13	294.27600000	1.13420000
14	304.60250000	17.51420000
15	317.82210000	25.51750000
16	335.25590000	8.29020000
17	364.87100000	17.31980000
18	373.69640000	16.81720000
19	421.24140000	2.03380000
20	440.73850000	6.66830000
21	480.27670000	1.88630000
22	547.77150000	1.24650000
23	591.31310000	97.16960000
24	652.96220000	2.32240000
25	676.46220000	5.59390000
26	701.35400000	17.62170000
27	727.65990000	2.69140000
28	755.23880000	9.69290000
29	792.39930000	10.30140000
30	820.98460000	35.15860000
31	848.59260000	26.60190000
32	854.55450000	29.14300000
33	896.04860000	35.17240000
34	948.50770000	36.22020000
35	958.75550000	1.96760000
36	973.56800000	10.85550000
37	983.56400000	3.22910000
38	1004.86630000	10.38560000
39	1038.07630000	2.44510000
40	1075.74260000	0.60300000
41	1105.33300000	29.64780000
42	1136.14170000	1.61190000
43	1148.74640000	4.18260000
44	1160.39980000	11.43970000
45	1210.25140000	8.09180000
46	1243.68500000	15.23900000
47	1251.78730000	4.80340000
48	1261.83700000	9.15970000
49	1282.56480000	1.39750000
50	1289.13390000	1.04790000
51	1306.40750000	0.20820000
52	1347.72800000	4.05240000
53	1363.86860000	201.24530000

54	1370.21460000	21.30980000
55	1403.29400000	12.84740000
56	1428.58640000	10.87160000
57	1442.99250000	23.19690000
58	1470.59460000	20.62100000
59	1472.55060000	19.84490000
60	1477.36070000	25.13640000
61	1489.25520000	5.35200000
62	1494.24050000	3.44630000
63	1505.83560000	8.41490000
64	1509.59130000	14.88610000
65	1523.34540000	24.51610000
66	1529.86360000	28.98000000
67	1541.70850000	48.48110000
68	1602.64930000	19.11910000
69	1754.48400000	507.07600000
70	3071.88750000	6.30840000
71	3073.70110000	3.77540000
72	3076.34760000	5.36660000
73	3082.00250000	18.57910000
74	3092.53150000	6.67040000
75	3111.73430000	10.33270000
76	3154.23100000	0.65730000
77	3159.35080000	6.72230000
78	3163.52820000	7.34910000
79	3179.06040000	6.59800000
80	3184.83950000	5.41910000
81	3192.11760000	18.30350000
82	3252.90030000	1.97860000
83	3271.34490000	2.07340000
84	3642.15860000	127.12840000

S41. HERCYNINE (2 + NA) (ISOMER B)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -829.16831346	a.u.
Gibbs Energy	: -828.96474800	a.u.
Number of imaginary frequencies	: 0	

S41.1. Cartesian Co-ordinates (XYZ format)

30

C	3.10177207	-0.83318102	1.07323205
C	1.95587695	-0.63584101	0.35029101
C	3.56740904	-0.64990801	-1.07586205
N	4.12117100	-0.84325403	0.14695799
H	5.09855604	-0.97756600	0.34357899
H	3.28022289	-0.98222297	2.12249804
N	2.26235795	-0.51850402	-0.98681402
C	0.53368098	-0.61775899	0.82858002
H	0.46578401	-0.19981200	1.83343005
H	0.17645000	-1.64396405	0.90170199
C	-0.44505200	0.06248500	-0.13780600
H	-0.05553800	-0.09578500	-1.14244998
N	-0.50523102	1.59867501	0.00479800
C	-1.83054900	-0.62926501	-0.09458700
O	-2.88521504	0.03322500	0.10468800
O	-1.78550100	-1.86206996	-0.29516101
C	0.87616402	2.18271995	-0.08403900
H	1.45786095	1.86815798	0.77391797
H	1.35157895	1.82627702	-0.99077803
H	0.78007698	3.26446009	-0.09237900
C	-1.11937296	2.03566003	1.30346596
H	-2.12913489	1.64982200	1.35123599
H	-0.51944900	1.65406299	2.12228394

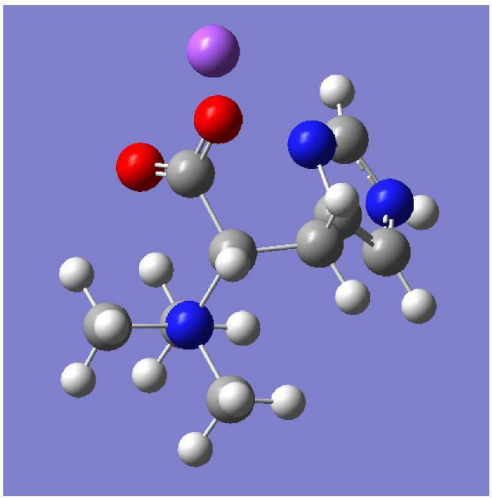
H	-1.11336505	3.12159395	1.32773995
C	-1.30180299	2.16725802	-1.13813996
H	-1.29328406	3.24987698	-1.05250704
H	-0.82448900	1.86683905	-2.06634402
H	-2.31128192	1.78291202	-1.07893598
Na	-4.02111292	-1.93561900	-0.13667400
H	4.14740705	-0.61042500	-1.98183596

S41.2. Frequencies

Mode	IR frequency	IR intensity
1	9.88910000	2.44500000
2	46.11400000	3.83850000
3	58.42890000	9.16680000
4	78.39470000	20.95180000
5	105.05460000	1.98610000
6	133.72410000	11.54300000
7	152.37370000	7.44890000
8	218.95270000	11.80780000
9	227.97400000	7.40300000
10	248.98060000	4.12120000
11	265.26340000	12.71270000
12	270.93540000	15.17400000
13	290.76420000	7.38560000
14	309.09290000	6.02230000
15	322.88890000	4.20540000
16	333.90330000	7.63250000
17	370.30530000	11.98910000
18	399.40500000	37.87700000
19	422.47040000	1.27100000
20	437.08780000	4.05490000
21	504.38230000	2.85320000
22	560.11750000	1.67290000
23	574.46030000	93.75620000
24	647.07020000	5.05790000
25	679.02570000	1.31360000
26	706.26960000	15.74470000
27	718.88540000	20.43140000
28	736.51990000	15.06030000
29	771.04660000	5.62060000
30	831.59210000	29.27860000
31	844.27460000	25.71880000
32	855.65650000	11.76020000
33	925.54100000	33.81650000
34	954.31480000	27.97410000
35	962.74090000	5.16910000
36	974.86430000	7.27160000
37	987.70970000	9.49070000
38	1005.51360000	21.55160000
39	1071.31600000	4.32790000
40	1080.44340000	0.25690000
41	1097.67480000	27.05430000
42	1137.95830000	4.38410000
43	1142.46650000	5.89050000
44	1157.63800000	5.92090000
45	1211.91850000	2.13790000
46	1247.23430000	2.44890000
47	1253.14770000	29.00410000
48	1276.27420000	0.07990000
49	1289.37010000	9.10670000
50	1299.60750000	6.29210000
51	1305.07610000	6.20500000

52	1335.44750000	3.18170000
53	1387.18120000	159.65450000
54	1392.08430000	3.07930000
55	1420.47770000	84.21270000
56	1436.59430000	10.33800000
57	1451.26410000	25.33010000
58	1460.78400000	25.25080000
59	1474.43320000	13.09310000
60	1479.48700000	2.03280000
61	1489.45170000	45.99110000
62	1496.63970000	10.51940000
63	1503.68640000	5.57980000
64	1510.43200000	8.55910000
65	1519.29900000	17.48050000
66	1522.44430000	22.27460000
67	1541.48000000	56.87220000
68	1592.91510000	16.01010000
69	1644.93950000	424.61650000
70	3056.59230000	11.36880000
71	3076.42510000	5.17150000
72	3080.32030000	3.31590000
73	3085.18960000	19.16170000
74	3088.23240000	18.76070000
75	3093.88760000	1.77560000
76	3157.74430000	2.81980000
77	3163.43020000	2.44930000
78	3170.68730000	4.01190000
79	3187.12370000	2.93490000
80	3196.09610000	0.94160000
81	3199.71010000	11.95520000
82	3253.11960000	1.07230000
83	3267.73100000	0.73380000
84	3644.91480000	104.03240000

S42. HERCYNINE (2 + NA) (ISOMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: C[N](C)(C)C(Cc1c[nH]cn1)C(=O)[O].[Na]	
Formula	: $C_9H_{15}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -829.17670870	a.u.
Gibbs Energy	: -828.96976900	a.u.
Number of imaginary frequencies	: 0	

S42.1. Cartesian Co-ordinates (XYZ format)

30

C	1.90746999	-1.98552895	0.35663101
C	1.27009106	-0.79341602	0.57238197
C	3.03961205	-0.35659000	-0.59462899
N	3.02590489	-1.69204605	-0.38725400
H	3.72162199	-2.34835196	-0.70001602
H	1.68142295	-2.98590302	0.67821002
N	1.99907398	0.22372000	-0.03083300
C	0.04279500	-0.58458602	1.40891397
H	0.30283201	0.05708100	2.25088096
H	-0.24676099	-1.54216599	1.83827198
C	-1.17498600	0.13328999	0.79267502
H	-1.87744701	0.32197699	1.60122502
N	-1.99939299	-0.69234699	-0.21449600
C	-0.70161998	1.50718296	0.26159000
O	-0.64614803	1.71371698	-0.97358900
O	-0.28103501	2.25036407	1.16904604
C	-2.54120111	-1.91358602	0.46126601
H	-1.72599399	-2.57784200	0.72262299
H	-3.08359003	-1.61670399	1.35424697
H	-3.21245408	-2.41889811	-0.22682901
C	-1.21841395	-1.11886799	-1.42720401
H	-0.80862999	-0.22766601	-1.88550699

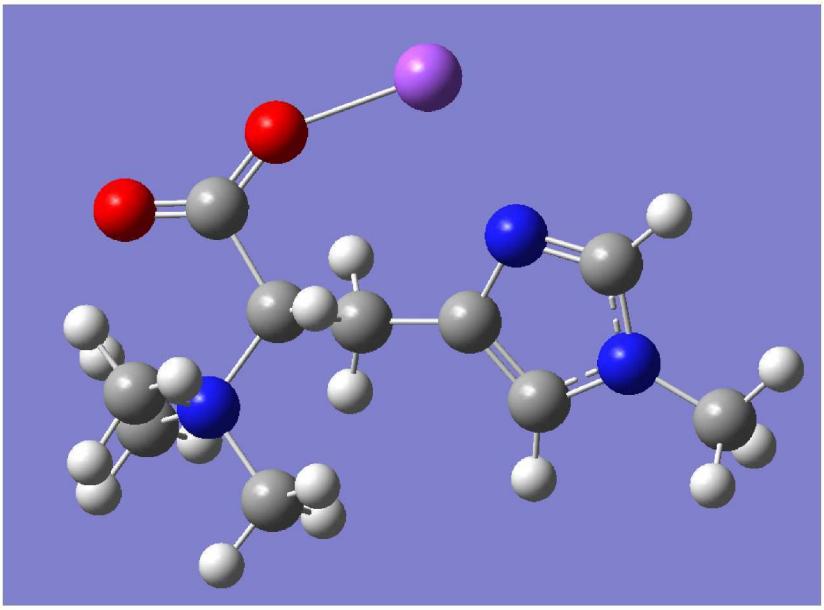
H	-0.42682201	-1.78919804	-1.11563504
H	-1.90248203	-1.63235402	-2.09719491
C	-3.16738296	0.14676100	-0.66192001
H	-3.79460406	-0.45993099	-1.30838501
H	-3.72805500	0.45531800	0.21589801
H	-2.78256512	1.00837600	-1.19314897
Na	1.41285896	2.60709906	-0.29419899
H	3.81826210	0.13736200	-1.15045500

S42.2. Frequencies

Mode	IR frequency	IR intensity
1	40.97540000	2.44630000
2	73.41750000	1.08900000
3	84.20770000	1.14290000
4	117.18590000	19.68080000
5	140.53230000	14.81730000
6	156.21750000	13.15060000
7	168.44090000	5.98840000
8	221.39510000	2.15980000
9	231.97470000	2.91420000
10	244.54620000	9.78140000
11	263.52290000	9.07770000
12	279.74120000	1.74950000
13	285.76660000	13.81190000
14	300.68310000	20.17890000
15	319.65330000	9.03140000
16	334.43380000	5.43710000
17	375.74200000	19.98890000
18	385.83390000	13.05480000
19	427.92150000	3.21750000
20	433.56800000	0.81690000
21	529.09190000	2.73860000
22	576.81500000	6.03060000
23	585.39050000	94.90990000
24	627.67160000	6.92900000
25	669.47830000	3.06010000
26	708.01670000	9.69430000
27	729.10490000	12.48640000
28	736.01350000	2.53960000
29	783.57910000	10.37790000
30	834.25990000	43.41610000
31	845.51150000	11.02990000
32	867.76430000	17.61860000
33	903.11380000	27.15020000
34	957.52630000	12.79510000
35	960.93560000	17.20820000
36	969.38910000	8.50640000
37	986.77410000	6.87670000
38	994.94480000	19.05030000
39	1046.01500000	5.12630000
40	1077.62830000	1.31630000
41	1106.15990000	27.33660000
42	1139.40390000	3.88350000
43	1147.89060000	2.22530000
44	1155.11850000	14.76390000
45	1210.66980000	21.70180000
46	1247.25980000	2.55400000
47	1253.04410000	7.46380000
48	1265.08040000	11.60150000
49	1293.15860000	0.44690000
50	1299.37050000	0.66440000

51	1312.42750000	2.97350000
52	1337.93790000	2.88000000
53	1369.89200000	60.46070000
54	1401.72270000	8.35120000
55	1413.79250000	75.36770000
56	1435.65680000	12.16770000
57	1446.96700000	12.02010000
58	1466.75820000	42.21720000
59	1471.94730000	17.26160000
60	1478.17940000	11.83650000
61	1485.91440000	18.76620000
62	1495.72250000	1.32720000
63	1505.63990000	4.32560000
64	1509.31400000	21.97740000
65	1523.31270000	19.08410000
66	1529.40250000	25.05100000
67	1542.00920000	48.42220000
68	1597.25710000	10.55420000
69	1682.82280000	388.06820000
70	3064.93230000	5.95030000
71	3073.95950000	4.12400000
72	3077.56360000	3.07780000
73	3082.99070000	22.62530000
74	3098.81280000	3.43960000
75	3101.17630000	10.93410000
76	3156.11880000	0.26180000
77	3161.40460000	5.67850000
78	3169.68480000	2.44900000
79	3179.36190000	5.68450000
80	3189.22580000	2.91090000
81	3196.17740000	7.94360000
82	3249.15830000	1.12370000
83	3267.70650000	2.29620000
84	3644.04320000	124.35190000

S43. METHYL-HERCYNINE (3 + NA) (ISOMER A)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)[O])[N](C)(C)C.[Na]	
Formula	: $C_{10}H_{17}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -868.49909087	a.u.
Gibbs Energy	: -868.26926300	a.u.
Number of imaginary frequencies	: 0	

S43.1. Cartesian Co-ordinates (XYZ format)

33

C	2.20797992	-1.17669797	-0.51875401
C	1.31601596	-0.13858500	-0.49635601
C	3.16003108	0.58376598	0.37183499
N	3.37674189	-0.70498198	0.03648200
H	2.12760806	-2.18217993	-0.89091498
N	1.93146706	0.96718198	0.06814600
C	-0.09274500	-0.11639400	-1.00080299
H	-0.24640600	-1.01058602	-1.60005498
H	-0.21441001	0.71987998	-1.68707597
C	-1.17578399	0.01252800	0.10272700
H	-0.69337797	0.03504400	1.07724202
N	-2.09330511	-1.22627699	0.19080500
C	-1.95361698	1.36757302	-0.05146900
O	-3.15365005	1.35812497	-0.30676401
O	-1.17589200	2.34386706	0.10471400
C	-1.27396500	-2.44509292	0.47428200
H	-0.61445999	-2.64918995	-0.36054400
H	-0.68939000	-2.27662611	1.37385499

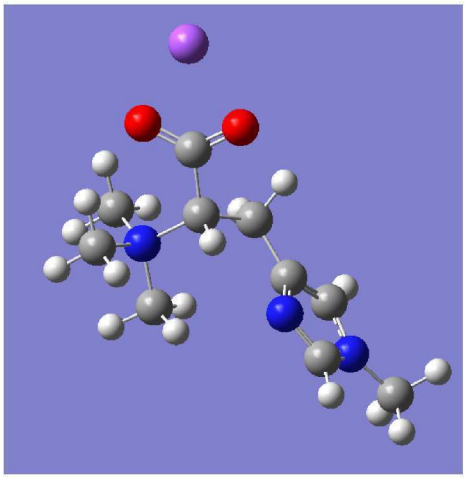
H	-1.94463503	-3.28710699	0.61934102
C	-2.88989401	-1.44257402	-1.06680202
H	-3.46952009	-0.54467702	-1.24526095
H	-2.21156001	-1.63659203	-1.89054406
H	-3.53008103	-2.30665588	-0.91321802
C	-3.04872298	-1.04025698	1.34146500
H	-3.64315104	-1.94418800	1.43725705
H	-2.46811604	-0.88122499	2.24586892
H	-3.67083311	-0.18062800	1.12691498
Na	0.80241698	3.03805399	0.27253199
H	3.92055297	1.19616604	0.82628000
C	4.61434698	-1.45314503	0.20841500
H	5.35457420	-0.80741102	0.67210501
H	4.44702816	-2.31665301	0.84909397
H	4.98969507	-1.78564894	-0.75730801

S43.2. Frequencies

Mode	IR frequency	IR intensity
1	24.04500000	6.70990000
2	39.08630000	1.24260000
3	65.70510000	2.93610000
4	79.85390000	3.17140000
5	92.46580000	18.65300000
6	103.59860000	5.27400000
7	125.67480000	1.20460000
8	167.19570000	11.49270000
9	188.05780000	4.35180000
10	206.23190000	9.50880000
11	219.41320000	11.97940000
12	239.95020000	7.84730000
13	250.46030000	0.57850000
14	266.83330000	0.22200000
15	292.41560000	0.27350000
16	302.34390000	16.97090000
17	322.95410000	20.24870000
18	334.55740000	2.96360000
19	339.69760000	10.72170000
20	364.34530000	24.13470000
21	411.07040000	3.45400000
22	423.06440000	2.64850000
23	441.39690000	5.22570000
24	482.19650000	1.29630000
25	547.42490000	1.50400000
26	622.21220000	4.33780000
27	645.47760000	17.06910000
28	683.33700000	1.79110000
29	710.08830000	15.06780000
30	747.86940000	11.72110000
31	757.65800000	13.78220000
32	789.19160000	8.74770000
33	822.36990000	33.19960000
34	843.84020000	28.04770000
35	854.13620000	31.66000000
36	897.06530000	35.40630000
37	949.67780000	34.85810000
38	973.68850000	12.48130000
39	981.16230000	3.37570000
40	1020.17640000	20.36570000
41	1039.05120000	3.46380000
42	1070.49420000	2.83240000
43	1075.97630000	0.51040000

44	1091.11170000	5.22870000
45	1136.24010000	2.00980000
46	1148.98450000	4.46940000
47	1152.33420000	0.03870000
48	1185.80160000	18.72900000
49	1215.46430000	15.74590000
50	1243.52830000	15.08180000
51	1253.41240000	6.76850000
52	1270.39720000	18.96500000
53	1282.39140000	1.69900000
54	1290.13970000	1.89990000
55	1327.15570000	23.54320000
56	1358.53280000	88.28550000
57	1367.47980000	119.06920000
58	1377.33800000	6.31750000
59	1402.10310000	12.95910000
60	1417.26930000	2.79430000
61	1428.51400000	11.50620000
62	1443.05530000	24.22730000
63	1461.64020000	15.94400000
64	1470.17550000	21.31240000
65	1477.12680000	21.87500000
66	1488.53530000	8.74510000
67	1488.80820000	10.49550000
68	1494.08900000	4.04040000
69	1505.17690000	8.38930000
70	1509.03360000	13.59260000
71	1518.23020000	11.23270000
72	1522.93050000	24.46380000
73	1541.34800000	45.96950000
74	1547.56740000	85.56490000
75	1599.64110000	6.63650000
76	1753.32910000	510.76650000
77	3057.82850000	20.11900000
78	3071.47400000	4.98200000
79	3072.62980000	5.31830000
80	3076.00060000	5.91540000
81	3081.52500000	18.27060000
82	3091.97360000	6.78350000
83	3110.36860000	10.82840000
84	3124.41390000	4.92080000
85	3148.50390000	2.72100000
86	3153.86660000	0.75100000
87	3159.08060000	6.78910000
88	3163.08080000	7.93280000
89	3179.20050000	6.49960000
90	3184.29120000	5.46050000
91	3191.71620000	18.03810000
92	3244.58240000	1.26410000
93	3261.44910000	2.01500000

S44. METHYL-HERCYNINE (3 + NA) (ISOMER B)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)[O])[N](C)(C)C.[Na]	
Formula	: $C_{10}H_{17}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -868.49796175	a.u.
Gibbs Energy	: -868.26934900	a.u.
Number of imaginary frequencies	: 0	

S44.1. Cartesian Co-ordinates (XYZ format)

33

C	-2.81360102	0.61010402	0.95935100
C	-1.63323700	0.44758299	0.28163999
C	-3.19923806	0.32095900	-1.18248200
N	-3.80928111	0.53109097	0.00989600
H	-3.03335690	0.78983301	1.99652600
N	-1.88928103	0.26258799	-1.05563402
C	-0.22865701	0.52320802	0.80666798
H	-0.16350500	0.10040800	1.80996501
H	0.05595900	1.57008195	0.89981002
C	0.81961399	-0.08395000	-0.13461301
H	0.43426499	0.03179400	-1.14690602
N	0.99713701	-1.60934496	0.02731800
C	2.14573693	0.71407503	-0.08144100
O	3.24993801	0.13325500	0.10604300
O	2.00545812	1.94216895	-0.26741499
C	-0.33578700	-2.29806900	-0.05288000
H	-0.94038397	-2.01594090	0.80060101
H	-0.83604503	-1.99100697	-0.96424198
H	-0.15728900	-3.36932993	-0.04487200
C	1.64179504	-1.98008597	1.33156598
H	2.62224388	-1.52409506	1.37051105
H	1.01794696	-1.62635398	2.14510393
H	1.71120703	-3.06322908	1.37478304

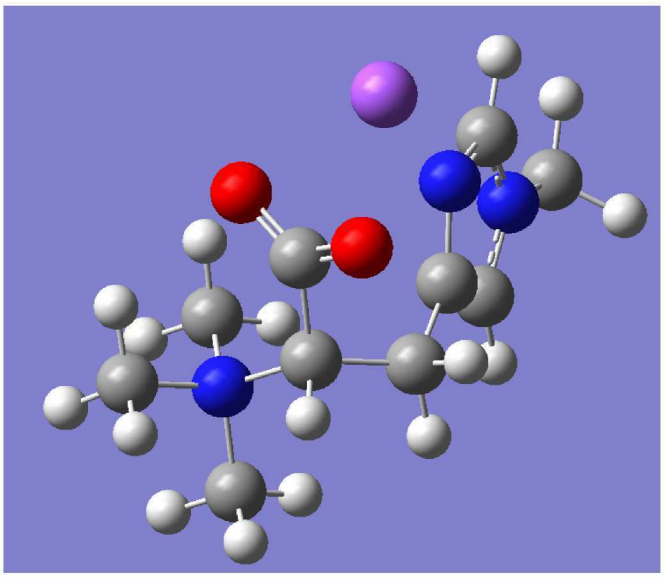
C	1.83514500	-2.13077593	-1.10817599
H	1.91266799	-3.20925093	-1.00581503
H	1.33441305	-1.88360596	-2.03970194
H	2.81089592	-1.66646898	-1.05700302
Na	4.22910118	2.18357301	-0.12192700
H	-3.75091100	0.21562099	-2.10149503
C	-5.23745584	0.66502702	0.24549200
H	-5.46698809	1.65375197	0.63913900
H	-5.76270390	0.53080201	-0.69610298
H	-5.57912493	-0.09074900	0.95062703

S44.2. Frequencies

Mode	IR frequency	IR intensity
1	9.17520000	2.55670000
2	36.13580000	2.29660000
3	55.48240000	7.50590000
4	75.62870000	16.33060000
5	84.56260000	5.81410000
6	99.98740000	1.91870000
7	129.10590000	7.98870000
8	146.72670000	6.75930000
9	168.63630000	10.82160000
10	215.61960000	10.68780000
11	222.30260000	0.18070000
12	252.47430000	7.80560000
13	261.57980000	6.45270000
14	275.71880000	11.33860000
15	292.51450000	8.93720000
16	301.96880000	4.83310000
17	311.75230000	6.43530000
18	330.52360000	4.40400000
19	363.70080000	10.83630000
20	388.74340000	5.28800000
21	400.24110000	37.32610000
22	428.73900000	2.28040000
23	440.53250000	2.34200000
24	508.78900000	2.79300000
25	559.48090000	1.43460000
26	631.58280000	8.88930000
27	648.53900000	7.67510000
28	677.37690000	5.37360000
29	702.68310000	19.67460000
30	733.58610000	16.68070000
31	755.29540000	23.32340000
32	765.99450000	4.98820000
33	833.48880000	27.20500000
34	838.73150000	25.57330000
35	855.99770000	13.77070000
36	925.99220000	33.33630000
37	955.26950000	29.67640000
38	974.74590000	9.75610000
39	1001.05640000	15.04920000
40	1005.88720000	18.12690000
41	1068.50930000	0.72840000
42	1075.03690000	7.82590000
43	1080.60240000	0.92540000
44	1084.50230000	9.94040000
45	1141.20540000	1.00690000
46	1151.18060000	0.69430000
47	1155.75830000	16.19940000
48	1178.24500000	13.46050000

49	1221.01200000	2.55390000
50	1248.08400000	7.95850000
51	1258.05740000	31.43510000
52	1276.46370000	0.03500000
53	1289.27130000	14.38880000
54	1300.75620000	12.95880000
55	1321.09130000	16.41220000
56	1357.80540000	15.03660000
57	1386.83440000	158.73060000
58	1396.84150000	5.14000000
59	1417.43430000	19.64400000
60	1421.79170000	69.64140000
61	1436.83990000	10.47890000
62	1451.14870000	25.07170000
63	1458.97770000	26.26880000
64	1475.09550000	15.85740000
65	1478.34950000	1.13690000
66	1488.80510000	6.42230000
67	1489.44380000	48.94750000
68	1497.09370000	10.74510000
69	1503.50520000	6.36950000
70	1510.20070000	7.98460000
71	1518.94230000	9.68850000
72	1520.78130000	20.54810000
73	1533.96720000	75.44440000
74	1541.64810000	50.60760000
75	1587.92810000	5.01810000
76	1643.22560000	423.72430000
77	3052.23980000	32.52060000
78	3054.64690000	13.22900000
79	3076.25920000	5.41680000
80	3079.81180000	4.00840000
81	3083.41640000	18.45380000
82	3087.26980000	21.95060000
83	3093.09480000	2.28020000
84	3115.03520000	8.08640000
85	3142.81160000	4.17830000
86	3157.44980000	2.88970000
87	3162.92180000	2.49220000
88	3170.45190000	4.05720000
89	3186.92030000	3.78650000
90	3196.62940000	1.09830000
91	3200.36470000	11.73660000
92	3243.91730000	1.06390000
93	3258.49080000	0.64580000

S45. METHYL-HERCYNINE (3 + NA) (ISOMER C)



Route	: # opt freq b3lyp/cc-pvtz geom=connectivity empiricaldispersion=gd3bj i	
	: nt=ultrafine pop=regular	
SMILES	: Cn1cc(nc1)CC(C(=O)[O])[N](C)(C)C.[Na]	
Formula	: $C_{10}H_{17}N_3NaO_2^+$	
Charge	: 1	
Multiplicity	: 1	
Energy	: -868.50715200	a.u.
Gibbs Energy	: -868.27509500	a.u.
Number of imaginary frequencies	: 0	

S45.1. Cartesian Co-ordinates (XYZ format)

33

C	2.08848500	-1.18490899	0.60115099
C	1.10098100	-0.24118800	0.71231502
C	2.71799588	0.65409797	-0.40371299
N	3.11197710	-0.60481000	-0.11212100
H	2.16158199	-2.18896198	0.97953999
N	1.51511204	0.91774398	0.07464500
C	-0.17988200	-0.38499901	1.47934794
H	-0.18406200	0.34503400	2.28891301
H	-0.18692800	-1.36363006	1.95631897
C	-1.51885200	-0.11230500	0.76442200
H	-2.29565001	-0.12081400	1.52568495
N	-1.97820795	-1.19691801	-0.22998300
C	-1.46508896	1.31736398	0.17490800
O	-1.40926802	1.47953796	-1.06696606
O	-1.34557998	2.19209790	1.05421400
C	-2.14612794	-2.49925590	0.48907501
H	-1.17963505	-2.85942888	0.82099098
H	-2.80488896	-2.35483193	1.34052896
H	-2.58342195	-3.21807289	-0.19758800

C	-1.03023899	-1.40059400	-1.38008201
H	-0.89848799	-0.44484201	-1.87135696
H	-0.08672000	-1.76679397	-0.99437898
H	-1.47375798	-2.13411808	-2.04779005
C	-3.32188797	-0.79180700	-0.77629298
H	-3.68375897	-1.59027505	-1.41735303
H	-4.00426817	-0.64642698	0.05638800
H	-3.19770789	0.12744799	-1.33510995
Na	0.24837901	2.97817206	-0.35563800
H	3.34146690	1.33441901	-0.95951098
C	4.38619280	-1.22057998	-0.45374000
H	4.97129107	-0.51704901	-1.03922498
H	4.93737316	-1.47347999	0.44994399
H	4.22432899	-2.12121701	-1.04263604

S45.2. Frequencies

Mode	IR frequency	IR intensity
1	39.99270000	2.29480000
2	55.33510000	0.67800000
3	75.10860000	0.35640000
4	88.90970000	2.00800000
5	109.12640000	16.54320000
6	134.94730000	5.58420000
7	156.04650000	30.33100000
8	163.08350000	1.77750000
9	182.00910000	1.67640000
10	209.90550000	5.00650000
11	223.32800000	2.98350000
12	253.64660000	3.02240000
13	263.38750000	6.74070000
14	276.02890000	1.97710000
15	293.32140000	21.83450000
16	301.57360000	9.96640000
17	323.90430000	8.42280000
18	331.60420000	6.30770000
19	350.58570000	2.04760000
20	377.17950000	28.00830000
21	412.43340000	1.66920000
22	430.35720000	1.55360000
23	434.63440000	1.72310000
24	528.24450000	2.14670000
25	567.75460000	1.86440000
26	606.96460000	3.86900000
27	646.37480000	21.68790000
28	703.83280000	11.94290000
29	706.25380000	7.96960000
30	728.45930000	13.16780000
31	745.63480000	0.38630000
32	778.57970000	9.03670000
33	833.82040000	45.47550000
34	841.21160000	10.94900000
35	868.29460000	18.94350000
36	903.24010000	27.76450000
37	960.82170000	27.77570000
38	971.08290000	8.76620000
39	992.73370000	10.77330000
40	998.13580000	19.92460000
41	1049.06360000	10.27990000
42	1072.50780000	2.55810000
43	1078.73640000	1.10440000
44	1090.24740000	5.22180000

45	1139.84630000	3.88290000
46	1147.34390000	6.87570000
47	1152.08540000	0.07340000
48	1185.11270000	17.30400000
49	1215.77050000	28.52010000
50	1247.69670000	3.00090000
51	1257.76170000	10.59760000
52	1272.02110000	16.81910000
53	1293.67240000	0.36640000
54	1303.10810000	3.38150000
55	1327.88330000	16.12360000
56	1354.97150000	29.11330000
57	1378.91010000	33.79760000
58	1397.00780000	12.29050000
59	1412.92760000	68.38170000
60	1420.22270000	9.50260000
61	1435.90660000	10.73730000
62	1447.08010000	12.29180000
63	1461.84940000	16.43940000
64	1467.78190000	35.15740000
65	1478.10500000	12.36550000
66	1485.86820000	17.15150000
67	1488.87710000	11.71020000
68	1495.99830000	1.60350000
69	1506.01460000	5.02710000
70	1509.05230000	21.23530000
71	1518.45990000	12.45530000
72	1523.63770000	19.24400000
73	1542.10110000	47.65980000
74	1546.77030000	68.36110000
75	1594.16200000	4.52480000
76	1682.41730000	384.88370000
77	3056.87440000	21.61250000
78	3064.28630000	6.10860000
79	3073.67840000	4.14470000
80	3077.20070000	3.63350000
81	3082.39240000	22.85860000
82	3097.66290000	4.02270000
83	3100.36040000	11.41100000
84	3122.85140000	5.25640000
85	3147.19250000	2.98390000
86	3155.73430000	0.27650000
87	3161.08950000	5.80280000
88	3169.12810000	2.36890000
89	3179.32450000	5.59640000
90	3189.13500000	2.87730000
91	3195.58350000	8.32640000
92	3240.48020000	0.70530000
93	3257.85570000	2.12490000